Int. J. Electrochem. Sci., 13 **(2018)** 2585 – 2595, doi: 10.20964/2018.03.34

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Dynamical Behavior of Electrochemical Noise Associated to Corrosion Resistance of Ti-6Al-4V Alloy

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Received: 14 November 2017 / *Accepted:* 3 January 2018 / *Published:* 5 February 2018

This research work presents the analysis of the dynamical behavior of electrochemical noise from Ti-6Al-4V alloy samples by reconstruction of recurrence plots (RP) and calculation of quantitative RP indexes. The aim was to evaluate the association between RP indexes and the corrosion resistance of Ti-6Al-4V. The study included electrochemical noise time series from 27 samples of Ti-6Al-4V alloy prepared under diverse conditions (milling time, sintered or green samples) and exposed to Hanks' or Ringer's solution. Voltage RP indexes were found to be different depending on the sintering method and type of exposure solution, but there were no differences among current RP indexes. Corrosion resistance were also correlated with RP indexes depending on type of sintering, solution and trend removal method. Voltage time series with polynomial trend removal had correlations with corrosion resistance only in the green samples exposed to Ringer's solution: high corrosion resistance was associated with less determinism (fewer diagonal lines but longer). In contrast, voltage time series with trend removal showed that corrosion resistance was associated with more stationary episodes (more trapping time and larger vertical lines). RP indexes may be useful to identify conditions of preparation and exposure that yield higher corrosion resistance to Ti-6Al-4V.

Keywords: Mechanical Alloying, Biomaterials, Recurrence Method, Electrochemical Noise, Corrosion.

1. INTRODUCTION

In the search for new biomaterials with better compatibility, the electrochemical noise method is a practical approach to assess the resistance to corrosion [1], where samples of the material are exposed to a solution that mimics the human body fluids (e.g. Hanks' solution or Ringer's), and recordings of the time series of current (I) and voltage (V) were obtained. These time series were analyzed with different indexes, for example the corrosion rate index (Rn) = standard deviation of voltage / standard deviation of current, which is an estimate of the corrosion rate [2]. Besides the many statistical and spectral methods to analyze I and V time series in order to assess resistance corrosion [2], other non-linear analysis methods have been proposed to evaluate the dynamical behavior [3]. The current work is based on the recurrence plot analysis by applying a non-linear method to different materials [4-5]. Recurrent plot analysis allows to evaluate the dynamical behavior of a time series through identification of similar data points that occurred at different time (recurrences), and the recurrence plots are able to exhibit different patterns that could be associated to deterministic behavior (e.g. periodic oscillations) or stochastic behavior (e.g. white noise). This qualitative evaluation of recurrence plots can be complemented with assessment of quantitative indexes [6].

The recurrence plot analysis of time series obtained from electrochemical noise has been previously applied to other materials such as AISI 304 stainless steel exposed to saline [3], UNS-S31603 stainless steel exposed to sea salt [7], and copper exposed to different salt solutions [5]. Further examples of qualitative changes in recurrence plots were observed in different preparation conditions [3], showing that the rate of determinism allows distinguishing different stages of fatigue damage [7], and that in the case of copper samples, a high determinism (about 90%) was associated with pitting (suggesting an electrochemical noise behavior of quasi-periodic type) whereas samples without pitting had determinism almost equal to 0% (indicating a stochastic behavior) [5]. Likewise, it has also been determined that hydrostatic pressure influencing the corrosion behavior of high strength steel Ni-Cr-Mo-V, because as the hydrostatic pressure increase, the corrosion resistance deteriorates [4]. Other study compared the AZ80 magnesium alloy with or without ultrasonic vibration solidification treatment (UVST), and showed that samples without UVST had higher recurrence percentage than those without treatment, implying that the electrochemical noise transients of the non-treated samples were more periodic than the UVST samples [5]. In order to demonstrate the feasibility of recurrence quantitative analysis (RQA) and detect flank wear in face milling, several recurrence plot indexes including trapping time showed changes for different flank wear [8]. Electrochemical noise could be considered a difficult electrochemical technique because the analysis of such small signal (several microvolts) requires a large number of mathematical algorithms [9-10]. Nevertheless, the method has the advantage of being a non-destructive technique. Therefore, this study was focused on the corrosion resistance of Ti-6Al-4V alloy samples with recurrence plot analysis in the light of new information for the electrochemical noise signals that may not be identified with other traditional methods [3, 5, 7, 11].

Ti-6Al-4V alloy possesses a desirable combination of attractive properties such as high melting point, high specific strength, fracture toughness, fatigue strength, good corrosion resistance, and excellent biocompatibility and is widely used in a variety of engineering applications [12]. In this work, the dynamical behavior of electrochemical noise recorded from Ti-6Al-4V alloy samples was analyzed by reconstruction of recurrence plots and calculation of several quantitative recurrent plot indexes. The aim was to evaluate the association between the recurrent plot indexes and the corrosion resistance of this alloy, estimated by Rn. Several preparation conditions (milling time, sintered or green samples) and exposure to solutions (Hanks' or Ringer's) were compared.

2. EXPERIMENTAL METHODS

2.1 Materials preparation and electrochemical test

Twenty seven Ti-6Al-4V samples of 1 cm^2 were prepared with different milling times (0, 3, 5 and 8 hours). Some samples underwent spark plasma sintering (SPS) and others had no sintering (green samples) [13]. Then samples were exposed to an electrochemical test with either Hanks' or Ringer's solution (Figure 1). A diverse number of samples and testing were obtained for each condition (Table 1). Electrochemical tests were performed on a Solartron Z device with 3 pairs of electrodes: the working electrode (with the sample of alloy Ti6Al4V), one of calomel and other one of platinum (used as reference). During each test, simultaneous time series of I and V were digitized at 1 sample per second (each time series comprised 2048 data points).

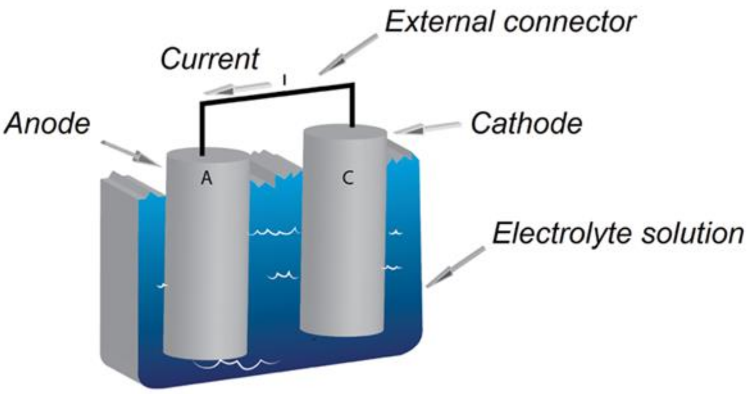

Figure 1. Diagram of the electrochemical test setup.

Table 1. Characteristics of Ti-6Al-4V alloy samples preparation and solution type (Ringer's or Hanks'). Each number corresponds to the number of samples with the same characteristic.

	Sintering Method				**Total samples**
	Green Samples		SPS		
Milling hours	Ringer's	Hanks'	Ringer's	Hanks'	
0	2	4	0	0	6
3	2	4	0	1	7
5	2	3	0	2	7
8	1	2	0	2	5
No milling	0	0	0	2	2
Total samples	7	13	0	7	27

2.2 Trend removal

The time series of I and V were analyzed using programs developed in Matlab version 8.0 (MathWorks Inc.), as described on a previous paper about the development and implementation of the computer programs [14]. The direct current (DC) trend of each time series was estimated by means of 3rd degree polynomial and also by a moving average filter with 21 points, which corresponds to a cut-off frequency of 0.02 Hz (Figure 2). Then the estimated trend was subtracted from the original trend to obtain the trend time series.

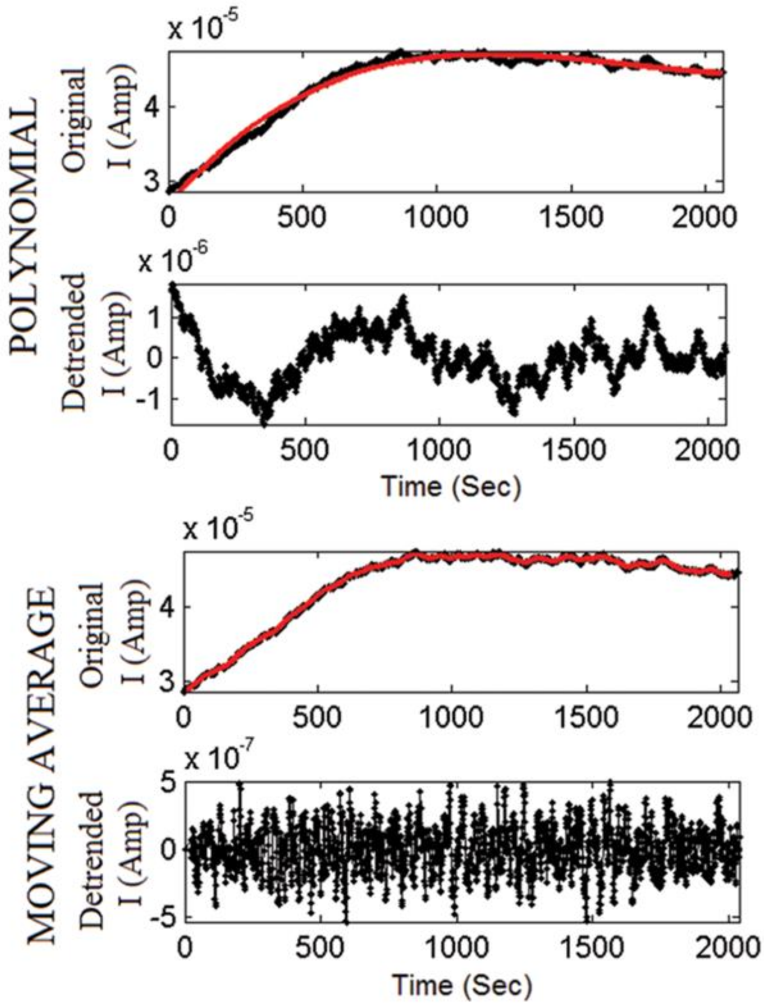

Figure 2. Example of DC trend removal with polynomial and moving average methods.

2.3 Recurrence plot analysis

Recurrent plot reconstruction and quantitative analysis was performed with the open access software crptool (available at http://tocsy.pik-potsdam.de/crp.php) [6]. The construction of the recurrence plot was based on a transformation of the time series to a phase space of dimension *m* by using a delay τ this transformation is called phase space embedding). The estimated τ value for each time series was obtained from the first zero crossing of the autocorrelation function, and *m* was estimated as embedding dimension when the false nearest neighbor function drops to zero (Figure 3).

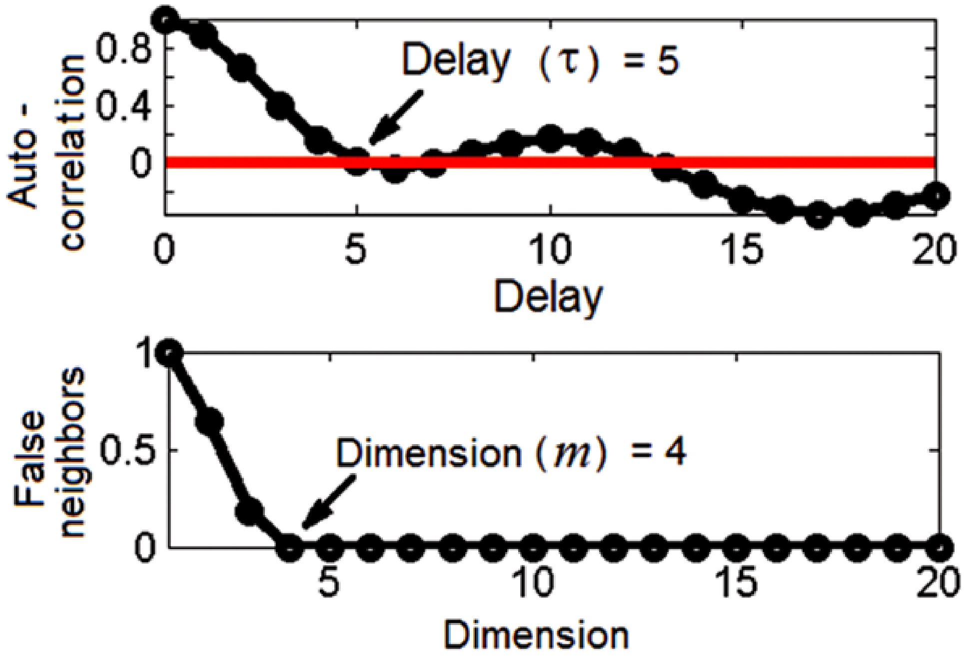

Figure 3. Example of phase space parameters estimation (dimension, m, and embedding delay, τ).

After reconstruction of the phase space with *m* and τ, each point on the recurrence plot ($R_{i,j}^{m,\varepsilon}$) was estimated as follows:

$$R_{i,j}^{m,\varepsilon} = \theta(\varepsilon - \| \bar{x}_i - \bar{x}_j \|), \bar{x}_i \in \Re^m, i, j = 1,..., \mathrm{N} \qquad (1)$$

where $\bar{x}_i = (D_i, D_{i+\tau}, ..., D_{i+(m-1)\tau})$ (2)

is the i-th embedding vector, and are the Heaviside function, the threshold in phase space, the norm or metric, embedding dimension, amount of embedding vectors, the i-th point of the time series and the embedding delay, respectively. The recurrence plot reconstruction was performed with threshold = 0.1 (using fixed recurrence rate = 10%), Euclidean norm, and the estimated *m* and τ. Figure 4 shows examples of time series and corresponding recurrence plots.

Recurrence plots were evaluated qualitatively (visual inspection) in order to describe the dynamical behavior of different sample types. Also, quantitative analysis was performed by calculation of the following recurrence plot indexes: percentage of determinism (percentage of recurrence points forming diagonal with respect to the total points of recurrence), mean diagonal length, maximum diagonal length, trapping time (time in which the dynamics remains trapped in a certain state) and laminarity (recurrence ratio of points forming vertical and horizontal lines) [6].

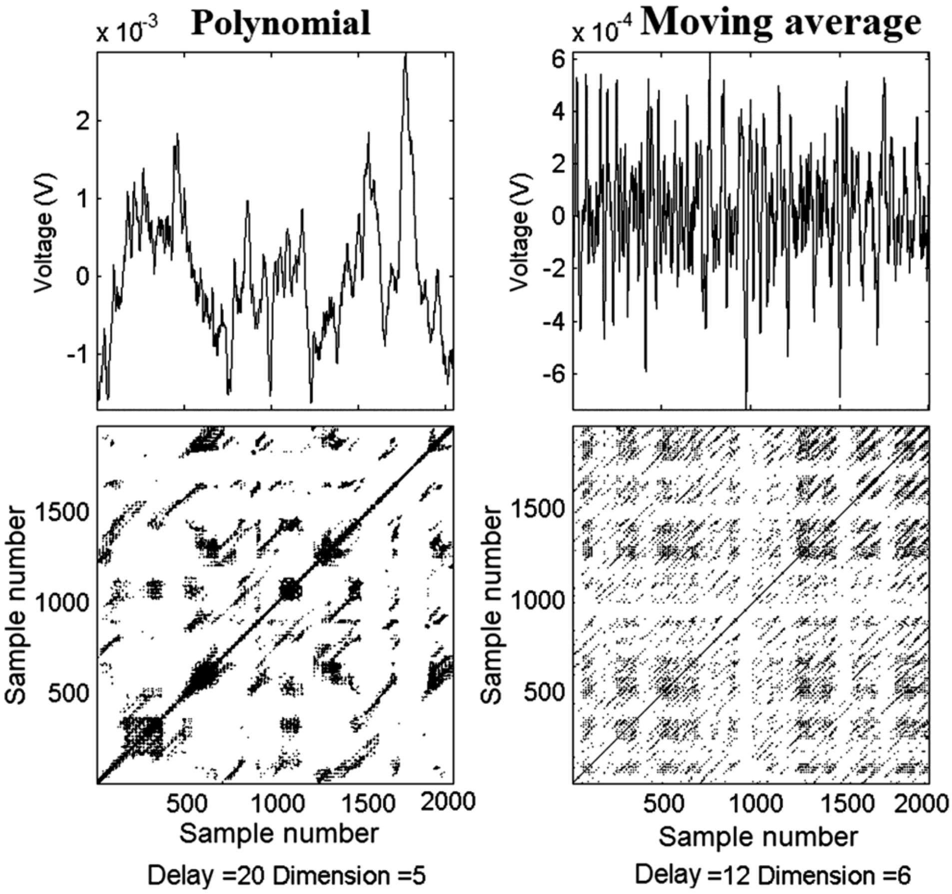

Figure 4. Examples of V time series and recurrence plots from a green sample of Ti-6Al-4V prepared with 3 hours of milling and exposed to Hanks solution.

2.4 Statistical analysis

Considering the small number of samples, normal distribution of data was not assumed, and the results are described as median (25th percentile – 75th percentile). Comparisons of medians between subgroups were performed with Mann-Whitney U tests, and correlation between Rn and recurrence plot indexes were calculated with the Spearman's method. Statistical analysis was performed using SPSS version 15.0 (StatSoft), and p-values < 0.05 were considered statistically significant.

3. RESULTS

The corrosion rate (Rn) as a function of milling time and different kinds of sintering and solutions is shown in Figure 5 (Panel A). There was no significant correlation between Rn and milling time. Rn values grouped with respect to sintering method and electrolyte solution (Panel B) showed that in the original data, SPS - Hanks samples had higher Rn than the other samples. The detrended data (with both methods) showed that Rn from SPS-Hank's samples was higher than Green-Ringer's samples but there were no significant differences in Rn between the Green-Hank's and Green-Ringer's samples.

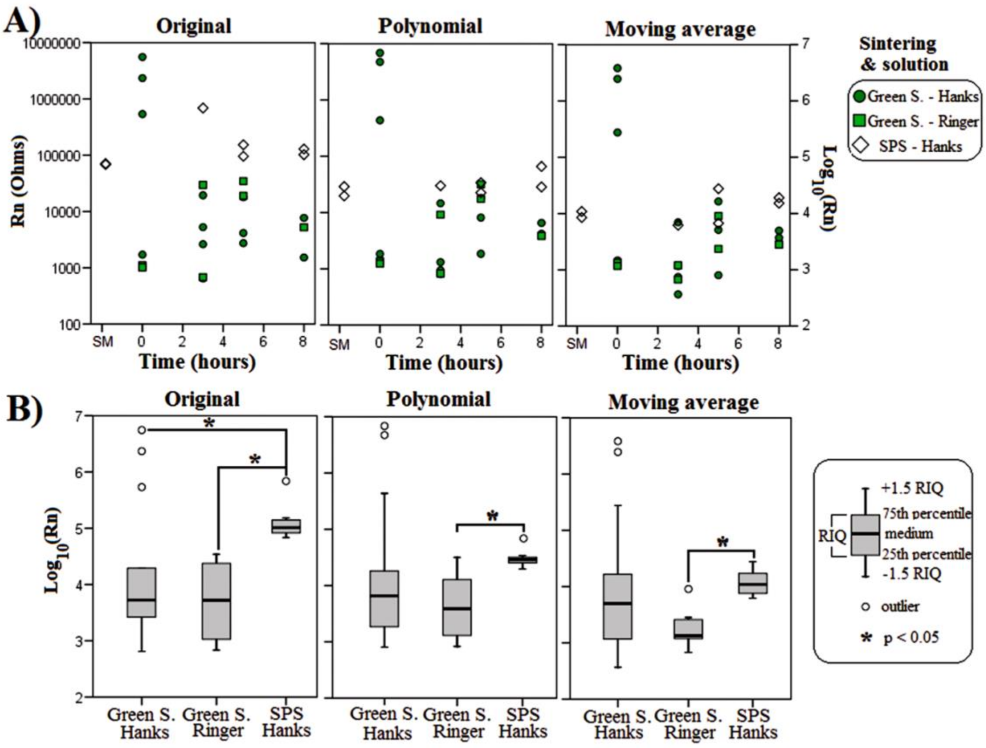

Figure 5. Estimates of noise resistance (Rn): A) Individual data as a function of time, B) Medium as a function of the sintering type and electrolyte solution. Rn data were estimated with the original series or after removal of trend (polynomial or moving average).

Table 2. Quantitative recurrence plot indexes of current time series compared by sintering method (Green or SPS) and solution (Hanks' or Ringer's). Samples from different milling times are grouped together. DC trend was removed by the polynomial method. Results are reported as median (25th percentile - 75th percentile).

	Green – Hanks' (N = 13)	Green – Ringer's (N = 7)	SPS – Hanks' (N = 7)
Determinism (%)	0.12 (0.12 – 0.17)	0.10 (0.09 – 0.18)	0.14 (0.12 – 0.17)
Mean diagonal	0.06 (0.05 – 0.10)	0.05 (0.05 – 0.07)	0.05 (0.04 – 0.05)*
Maximum diagonal	0.27 (0.16 – 0.66)	0.18 (0.12 – 0.35)	0.08 (0.07 – 0.17)*
Trapping time	0.06 (0.06 – 0.12)	0.06 (0.06 – 0.08)	0.05 (0.05 – 0.06)*
Maximum vertical	0.52 (0.29 – 0.80)	0.28 (0.22 – 0.55)	0.13 (0.11 – 0.22)*
Laminarity	0.015 (0.011 – 0.018)	0.013 (0.011 – 0.017)	0.011 (0.011 – 0.012)*

The recurrence plot indexes of current (I) time series from samples grouped by type of preparation (gathering all milling times in each group) are shown in Table 2 (DC trend was removed with the polynomial method). Compared with the subgroup of green samples and Hank's solution, time series from SPS-Hank's had smaller diagonals (mean and maximum), trapping time, vertical lines, and laminarity. Results of recurrence plot indexes of I time series after DC removal with moving average were not different between subgroups (data not shown).

The recurrence plot indexes of *V* time series from samples grouped by type of preparation (gathering all milling times in each group) are shown in Table 3 (DC trend was removed with the moving average method). Compared with the subgroup of green samples and Hanks solution, the green samples and Ringer's solution showed smaller diagonals, vertical lines and laminarity. On the other side, compared with the green samples and Hanks solution, SPS-Hank's samples had smaller diagonals and trapping time. Results of recurrence plot indexes from V time series after DC removal with the polynomial method were not different between subgroups (data not shown).

Table 3. Quantitative recurrence plot indexes of *voltage time series* compared by sintering method (Green or SPS) and solution (Hanks' or Ringer's). Samples from different milling times are grouped together. DC trend was removed by the moving average method. Results are reported as median (25th percentile - 75th percentile).

	Green – Hanks' (N = 13)	Green – Ringer's (N = 7)	SPS – Hanks' (N = 7)
Determinism (%)	0.18 (0.17 – 0.18)	0.18 (0.17 – 0.19)	0.18 (0.18 – 0.19)
Mean diagonal	0.12 (0.10 – 0.14)	0.06 (0.06 – 0.09)*	0.07 (0.05 – 0.08)*
Maximum diagonal	1.14 (0.96 – 1.40)	0.61 (0.48 – 1.03)*	0.75 (0.45 – 0.92)*
Trapping time	0.13 (0.10 – 0.18)	0.07 (0.06 – 0.11)	0.08 (0.07 – 0.10)*
Maximum vertical	1.06 (0.65 – 1.36)	0.40 (0.35 – 0.77)*	0.50 (0.36 – 0.77)
Laminarity	0.019 (0.016 – 0.020)	0.016 (0.015 – 0.018)*	0.016 (0.015 – 0.019)

Table 4. Spearman correlation coefficients between Rn and quantitative recurrence plot indexes from time series after DC trend removal by polynomial method. Significant correlations ($p < 0.05$) are indicated by asterisk (*).

	All (N = 27)	Green – Hanks' (N = 13)	Green – Ringer's (N = 7)	SPS – Hanks' (N = 7)
Voltage time series				
Determinism (%)	-0.31	-0.53	-0.79*	-0.321
Mean diagonal	0.16	0.26	0.79*	-0.321
Maximum diagonal	0.13	0.19	0.75	-0.321
Trapping time	0.20	0.23	0.75	-0.321
Maximum vertical	0.08	-0.02	0.46	-0.464
Laminarity	0.16	0.15	0.75	-0.429
Current time series				
Determinism (%)	0.20	0.19	-0.57	0.643
Mean diagonal	-0.19	-0.13	0.46	0.143
Maximum diagonal	-0.07	0.03	0.07	0.286
Trapping time	-0.27	-0.14	0.36	0.143
Maximum vertical	-0.24	-0.20	0.36	0.393
Laminarity	-0.25	-0.16	0.07	0.143

Table 4 shows Spearman's correlations between Rn and recurrence plot indexes from time series with DC trend removal by the polynomial method. Significant correlations between Rn and determinism and mean diagonal length were observed in the *V* time series, but there were no correlations in *I* time series. In contrast, Spearman's correlations between Rn and recurrence plot indexes from *V* time series with DC trend removal by the moving average method (Table 5) were significant for other indexes: transient time, maximum vertical lines and laminarity (all samples), maximum vertical lines (green samples- Hanks'), transient time and maximum vertical lines (green samples – Ringer's). Regarding I time series with DC trend removal by moving average (Table 5), there was correlation of Rn only with the maximum diagonal length (green-Hanks).

Table 5. Spearman correlation coefficients between Rn and quantitative recurrence plot indexes from time series after DC trend removal by moving average. Significant correlations ($p < 0.05$) are indicated by asterisks (*).

	All (N = 27)	Green – Hanks' (N = 13)	Green – Ringer's (N = 7)	SPS – Hanks' (N = 7)
Voltage time series				
Determinism (%)	-0.33	-0.36	-0.75	0.46
Mean diagonal	-0.02	0.03	0.46	-0.64
Maximum diagonal	-0.02	0.17	0.21	-0.57
Trapping time	0.42*	0.55	0.86*	-0.50
Maximum vertical	0.47*	0.63*	0.93*	-0.25
Laminarity	0.40*	0.51	0.46	0.14
Current time series				
Determinism (%)	-0.23	-0.37	-0.39	-0.11
Mean diagonal	-0.33	-0.44	-0.04	0.14
Maximum diagonal	-0.31	-0.62*	-0.11	0.00
Trapping time	0.08	0.06	0.29	-0.21
Maximum vertical	0.13	0.05	0.75	-0.36
Laminarity	-0.16	-0.09	-0.36	0.14

4. DISCUSSION

The current research work presents the analysis of recurrence plots electrochemical noise from biomaterial Ti-6Al-4V. From the experimental results, it was found that electrochemical noise samples prepared without sintering (green samples) and exposed to Hank's solution had a different dynamic behavior compared to green subsamples exposed to Ringer's solution and the samples with sintering by SPS method exposed to Hanks' solution (Table 2). In general the Green samples – Hanks' appear to have more deterministic behavior (longer diagonal lines) and moments where the signal remains bounded within the same range of values (larger laminarity and trapping time). This suggests that the samples in green – Hanks' have a more deterministic behavior (less random) than other subgroups of samples [7]. The corrosion rate, estimated through Rn in the current study, showed significant statistical correlation with several recurrence plot indexes, which were influenced by the method for

DC trend removal. Voltage time series with polynomial DC trend removal had correlations with Rn only in the Green samples exposed to Ringer's solution: high Rn was associated with fewer diagonal lines (i.e. less determinism) that were longer (i.e. average length). In contrast, voltage time series with DC trend removal by moving average of the same samples showed that Rn was associated with more stationary episodes (i.e. more trapping time and larger verticals).

In the current pilot study, the number of samples with different conditions was small. Further studies are needed to confirm these findings. In contrast with recurrence analysis of electrochemical noise from previous studies [3, 7, 9, 14], the current work included two different methods for DC trend elimination. The results showed that this simple signal processing step may affect the characteristics of the observed dynamic behavior, which highlights the importance of explicitly reporting the method used for DC trend elimination. Although Rn values cannot generally be related to corrosion rate in circumstances where the data set is non-Gaussian [15], in the absence of any other corroborative technique, we have used this approach as the best that we have available. Another important methodological issue is the selection of parameters for the phase space reconstruction (m, τ and ε). In the current work, the methods used for estimation of m and τ are well known and accepted for the estimation of the size and time delay. A value of 0.1 (corresponding to 10%) was chosen for ε [16]. However, further investigation is necessary to identify the optimal ε value for these particular time series, given the influence of ε on the density points within the recurrence plot and the assessment of quantitative recurrence plot indexes. Recurrence plot analysis and other methods developed for analysis of non linear systems have been used to understand corrosion in other alloys [17]. Although the corrosion resistance of Ti and Ti-6Al-4V alloys have been characterized with other conventional techniques [18], the electrochemical technique applied here provides a new insight information about Ti-6Al-4V samples reported previously [14, 19], and all coincide that Ti and Ti-6Al-4V permits excellent biocompatibility in the body human or similar conditions to the human body [16, 20].

5. CONCLUSIONS

The recurrence plot analysis of electrochemical noise from Ti-6Al-4V samples showed that the dynamic behavior of the time series was associated with the corrosion resistance (Rn) depending on the following factors: sintering type, solution type to which the sample is exposed, and the method used for DC trend elimination. These indexes may be useful to identify conditions of preparation and exposure that yield higher corrosion resistance to Ti-6Al-4V.

ACKNOWLEDGEMENTS
The authors thank the Consejo Nacional de Ciencia y Tecnología (CONACyT) for granting a M.Sc. scholarship to J.C. Betancourt-Ruiz, supporting a research stay at the Instituto Nacional de Cardiología Ignacio Chávez.

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