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ORIGINAL PAPER

Analysis of the dynamics of Intergranular corrosion process of sensitised 304 stainless steel using recurrence plots

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Abstract This study presents the assessment of the dynamics of intergranular corrosion of austenitic stainless steel with different degrees of sensitization through the analysis of electrochemical current noise signals. Samples of S30400 stainless steel were aged at 923 K for 50, 250 and 1,000 min before being quenched in water. The double Loop Electrochemical Potentiokinetic Reactivation test was applied to assess the degree of sensitization. The electrochemical noise data were analysed using a novel mathematical tool named Recurrence Plots (RP). This method allowed us to assess the dynamics of the intergranular corrosion process of the steel in a $H_2SO_4 + KSCN$ solution at room temperature. The study was conducted using a recurrence quantification analysis (RQA) from which it was possible to determine the percent of recurrence (%R), the percent of determinism (%D) and the information Entropy of the corrosion process. It was found that these parameters increased with the sensitisation intensity, which indicates that sensitisation induced a more deterministic dynamics on the electrochemical process.

Keywords Sensitisation · Stainless steel · Recurrence plots · Electrochemical noise

1 Introduction

Austenitic stainless steels are essentially iron–chromium–nickel alloys, containing between 18 and 30 wt% chromium, 8–20 wt% nickel and 0.03–0.1 wt% carbon [1]. The UNS S30400 austenitic stainless steel (S30400 SS) is used in a wide range of applications due to its acceptable corrosion resistance in non-chloride containing environments and good weldability. This kind of steel loses its corrosion resistance when is cooled slowly from the solution anneal temperature around 1,273 K (1,000 °C) or is reheated in the range from 823 K (550 °C) to 1,123 K (850 °C). In this temperature range there is a tendency to precipitate chromium-rich carbides as the alloy enters the carbide plus austenite phase field [2, 3]. Precipitation of carbides such as $M_{23}C_6$ and M_7C_3 occurs primarily at the austenite grain boundaries which are heterogeneous nucleation sites. The chemical composition in the vicinity of the grain boundaries can be altered by the precipitation of the chromium-rich particles [1]. This phenomenon is called sensitisation and prompts the resulting chromium-depleted zones at the grain boundaries to be susceptible to intergranular corrosion which is a well known case of localised corrosion [2, 4]. The effect of sensitisation on the corrosion resistance of stainless steels is difficult to determine quantitatively using conventional polarisation electrochemical methods, owing to the negligible weight loss involved. The microscopic dimension of the chromium depleted zone next to the grain boundaries is overshadowed by the unaffected bulk of the grains in many conventional corrosion tests. Several electrochemical methods have been proposed and used to evaluate sensitisation. One of the most utilised is the electrochemical potentiokinetic reactivation test (EPR) based on Cihal's method [5–7]. Due to its quantitative nature and reproducibility, this method has been

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standardized by ASTM to estimate the sensitization grade of AISI type 304 and 304L stainless steels [8].

Majidi et al. [9], proposed the double loop electrochemical potentiokinetic reactivation method (DLEPR) for determining the sensitization grade of stainless steels. This author compared the results of the new method, the single loop and the acid test, and concluded that: the agreement between measurement made with double loop and single loop EPR test was good and gave a quantitative measure of sensitization, which is based on the ratio of active peak currents on the forward and reverse scans Ir/Ia. The reproducibility of the double loop test, relies upon the use of optimum experimental conditions. They determined that the optimum DLEPR test conditions consist of a 0.5 M $H_2SO_4 + 0.01$ M KSCN solution and a scan rate of 100 mV min^{-1}.

On the other hand, it is known that electrochemical micro-cells form on the surface of metals undergoing corrosion which induce potential and current fluctuations. These electrochemical fluctuations are known as Electrochemical Noise (EN) and definitively contain information about faradaic processes taking place on the electrified interface formed by a metal in contact with an electrolyte.

Several parameters are usually obtained from EN measurements which depend upon the method used to analyse the data [10–12].

The localization index (LI) is a parameter defined as the current noise standard deviation (σI) to current Root Mean Square (I_{RMS}) ratio: $\sigma I{:}I_{RMS}$ [11].

$$\mathrm{LI} = \frac{\sigma_I}{I_{RMS}} = \frac{\sigma_I}{\sqrt{\sigma_I^2 + {<}I{>}^2}} \qquad (1)$$

This parameter will have values between 0 and 1. Values close to zero are an indication that a corrosion process tends to be uniform whereas values close to 1 suggest localised corrosion attack.

Chaos Theory has been applied in the characterization of various systems, including electrochemical processes [13]. Application of this deterministic theory to materials science revealed the prevalence of nonlinear dynamic effects on the behaviour of materials [14]. The application of this methodology to analyse the behaviour of electrochemical process allowed evaluating properties that could not be assessed otherwise [15–18].

Visual recurrence analysis is another approach to study the behaviour of nonlinear dynamical systems. This procedure has been used to differentiate between stochastic and chaotic variability. The principal instruments of the recurrence analysis are the Recurrence plots (RPs) which are especially useful for the graphical representation of multidimensional dynamic systems [19–21]. RPs are a valuable tool for assessing the geometry of the dynamics exploiting non-linear dependencies even in non-stationary time-series. These plots disclose distance relationships between points on a dynamical system providing a faithful representation of the time dependencies (correlations) contained in the data [19]. This is a graphical tool for the diagnosis of drift and hidden periodicities in the time evolution of dynamical systems, which are unnoticeable otherwise. RP's are graphical tools elaborated by Eckmann et al. based on Phase Space Reconstruction [19]. The RP method was introduced to visualize the time dependent behaviour of the dynamics of systems, which can be pictured as a trajectory in the phase space [22, 23] and represents the recurrence of the m-dimensional phase space trajectory $\vec{x}_i$. They are a graphical representation of the N × N-matrix:

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

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), $\|\bullet\|$ is the norm of vectors, $\Theta(\cdot)$ is the Heaviside function and N is the number of states.

One assigns a *''black''* dot to the value one and a *''white''* dot to the value zero. The two-dimensional graphical representation of $R_{i,j}$ then is called a RP.

There are two different types of RPs: unthresholded recurrence plots (UTRP) and thresholded recurrence plots (TRPs). An unthreshold RP is not binary but its matrix $R^u_{i,j}$ is given by the (real valued) distances of the vectors $\vec{x}_i$ and $\vec{x}_j$. The matrix then is usually represented in a two dimensional coloured plot. It has been shown that from an unthreshold RP it is possible to reconstruct time series [24]. However unthreshold RPs are more difficult to quantify than binary RPs. For this reason, in data analysis usually binary RPs are used.

The basic idea to keep in mind when studying RPs is simple: If the underlying signal is truly random and has no structure, the distribution of colours over the RP will be uniform, and so there will not be any identifiable patterns. On the other hand, if there is some determinism in the signal generator, it can be detected by a characteristic distinct distribution of colours. Considering this, the length of diagonal line segments of the same colour on the UTRP can give an idea about the signal predictability. This way it is possible to visualize and study (qualitatively) the motion of the system trajectories and infer some characteristics of the dynamical system that generated the time series.

Recurrence plots contain subtle patterns that are not easily ascertained by qualitative visual inspection. Zbilut and Webber have presented a recurrence quantification analysis (RQA) to quantify an RP [22, 24]. The RQA parameters proposed by these authors are:

The percent recurrence (%R), quantifies a percentage of the plot occupied by recurrent points. It quantifies the number of time instants characterized by a recurrence in the signals interaction: the more periodic the signal dynamics, the higher the %R value.

The percent determinism (%D), quantified 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.

The entropy Recurrence (ER) comes from the Shannon's information theory which quantifies the diagonal line segment distributions; by means of the following equation:

$$\mathrm{ER} = -\sum_{i=2}^{N} pi \log_2 pi \tag{3}$$

where pi is the probability that a diagonal of i-point length, with index i ranging from 2 to the maximum possible diagonal line length (which corresponds to the total number of points of the analyzed time series). pi is defined as the ratio between the number of i-point long diagonals, and the total number of diagonals. ER is measured in bits of information, because of the base-2 logarithm in this equation. Thus, whereas %D accounts for the number of the diagonals, ER quantifies the distribution of the diagonal line lengths. Large differences in the length of the diagonals require a more complex deterministic structure of the RP. A more complex dynamic will require a larger number of bits (ER) to be represented.

The objective of this study was to determine the change in the dynamics of the intergranular corrosion of stainless steel USN S30400 as a function of the degree of sensitization by means of electrochemical noise measurements applying the methodology of RP to analyse the data. Electrochemical noise is a non-intrusive technique compared with the Double Loop Electrochemical Potentiokinetic Reactivation Method as the measurements are carried out at open circuit potential.

2 Experimental

2.1 Sensitisation heat treatment

The material used in this study was a type-304 austenitic stainless steel (304 SS). The chemical composition (wt.%) was 18.38 Cr, 9.07 Ni, 0.39 Si, 1.4 Mn, 0.019 C, 0.025 P, 0.001 S. Rod steel samples of 1.5 cm diameter and 5 mm thick were subjected to sensitisation heat treatment at 923 K for 50, 250 and 1,000 min. Once the treatment period was completed the samples were quenched in air. Three samples were solution annealed at 1,323 K for 30 min and quenched in water at 273 K to eliminate any carbide precipitation in order to have samples with consistent metallurgical and electrochemical properties to be used as reference material for the study. The intention of using different aging times was to induce different degrees of sensitisation as it is known that this phenomenon depends upon temperature and time [9, 25, 26].

2.2 DLEPR tests

After heat treatment the surface of the samples were prepared by grinding them from 320 to 800 grit SiC paper, washed with distilled water, cleaned with acetone to eliminate grease and dried with air.

The DLEPR measurements were carried out using a conventional three electrode electrochemical cell in 0.5 M H_2SO_4 + 0.01 M KSCN solution. A treated SS sample acted as working electrode, a saturated calomel electrode (SCE) was the reference electrode and a graphite bar was the auxiliary electrode. The potentiokinetic reactivation was performed using a scan rate of 100 mV min^{-1} in a potential range from −420 mV to the return potential of 300 mV. All potentials reported in this work are referred to the SCE. The tests were conducted using a Gill ACM Instruments automated Potentiostat, Galvanostat and Zero Resistance Ammeter controlled by a PC.

2.3 Electrochemical noise tests

The electrochemical current noise test involved the use of two similar electrodes immersed within the electrolyte which was the same used for the DLEPR tests, (0.5 M H_2SO_4 + 0.01 M KSCN solution). All tests were conducted at room temperature. Stainless steel samples with different sensitisation degree acted as the working electrode one (WE1) while the sample subjected to solution annealing which presented no sensitization was the working electrode

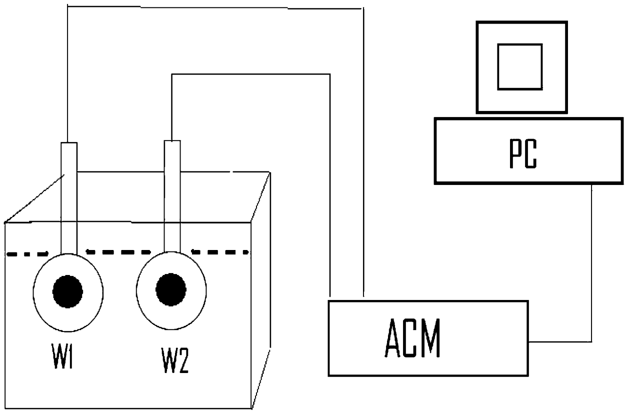

Fig. 1 Schematic of experimental set-up to perform EN measurements

two (WE2). A schematic of the electrochemical noise measurement setup is shown in Fig. 1.

The fluctuations in current were measured every 0.5 sec ($\Delta t = 0.5$) generating a total of 2,048 data per test. The frequency domain corresponding to the sampling conditions was evaluated to be between 1 Hz (f_{max}) and 0.9 mHz (f_{min}), from $f_{max} = 1/2\Delta t$ where Δt is the sampling interval and $f_{min} = 1/N\Delta t$ where N is the total number of data points. The samples were immersed in the electrolyte for 30 min at open circuit potential after which the electrochemical noise measurements were conducted using the same equipment than for the DLEPR tests.

3 Results and discussion

3.1 Sensitisation of the SS samples

The microstructure of the 304 SS samples after the sensitisation heat treatment presented changes in the appearance of the austenitic grain boundaries as shown in Fig. 2. The sensitised areas were characterised by a high frequency of grooved grain boundaries as the ageing treatment time was longer. The metallographic examination and determination of the sensitisation degree in quantitative terms is not reliable even there are several standard methodologies proposed in literature [6, 8]. This is the reason why electrochemical techniques are used to study this phenomenon providing quantitative assessments as in fact was corroborated in the present study by the results obtained from the DLEPR measurements as discussed next.

3.2 DLEPR tests

The results of the DLEPR tests are presented in Fig. 3 which show the polarization curves for the sample solution annealed and samples heat treated for 50, 250 and 1,000 min at 923 K. The sensitization intensity was evaluated from the value of the ratio Ir/Ia, where Ia is the peak current of the anodic scan and Ir is the peak current in the reversed scan. The sensitization intensity determined as the Ir/Ia ratio were <<<1 for the solution annealed sample, 0.068, 0.113 and 0.46 for the sample treated for 50, 250 and 1,000 min, respectively. The susceptibility of 304 SS to suffer sensitization as a consequence of heating in a temperature range from 723 to 1,123 K is well documented [1–4]. The application of electrochemical techniques such as the EPR and DLEPR to evaluate the sensitisation degree and susceptibility of SS to undergo intergranular corrosion has also been reported by several authors [6–9, 25–27]. The images of the microstructure of the steel in Fig. 2 show changes in the grain boundaries of the austenite. The results from DLEPR tests showed that as the heat treatment period increased the sensitisation degree also increased.

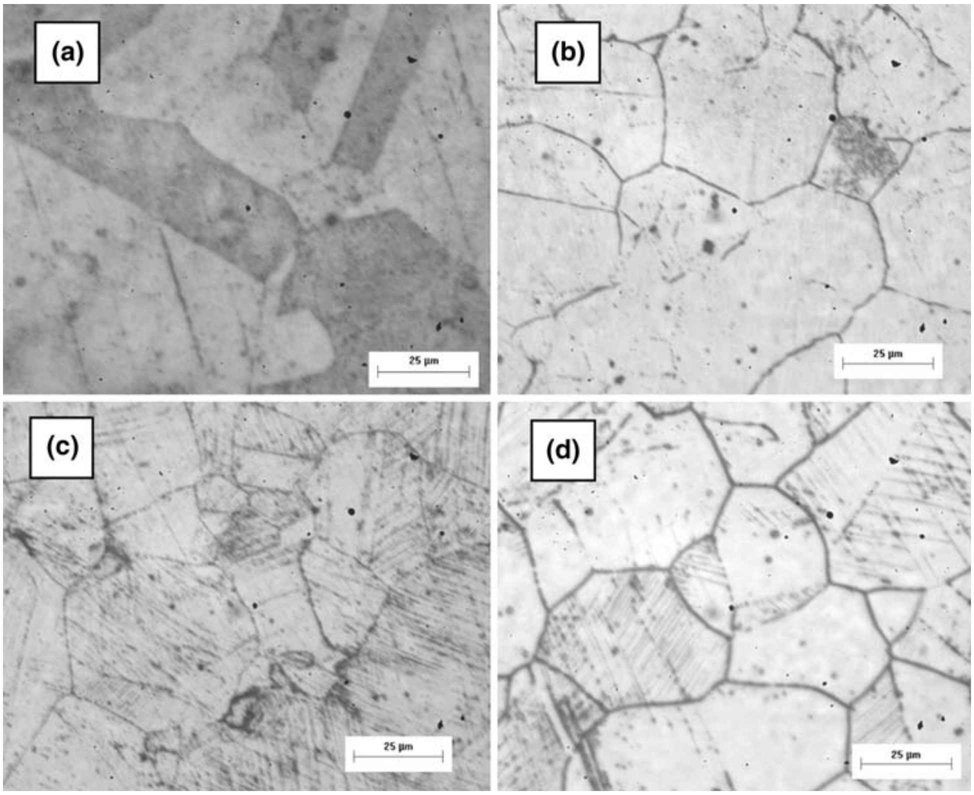

Fig. 2 Microstructures of samples subjected to: **a** solution annealing, **b** heat treated for 50 min, **c** heat treated for 250 min and **d** heat treated for 1,000

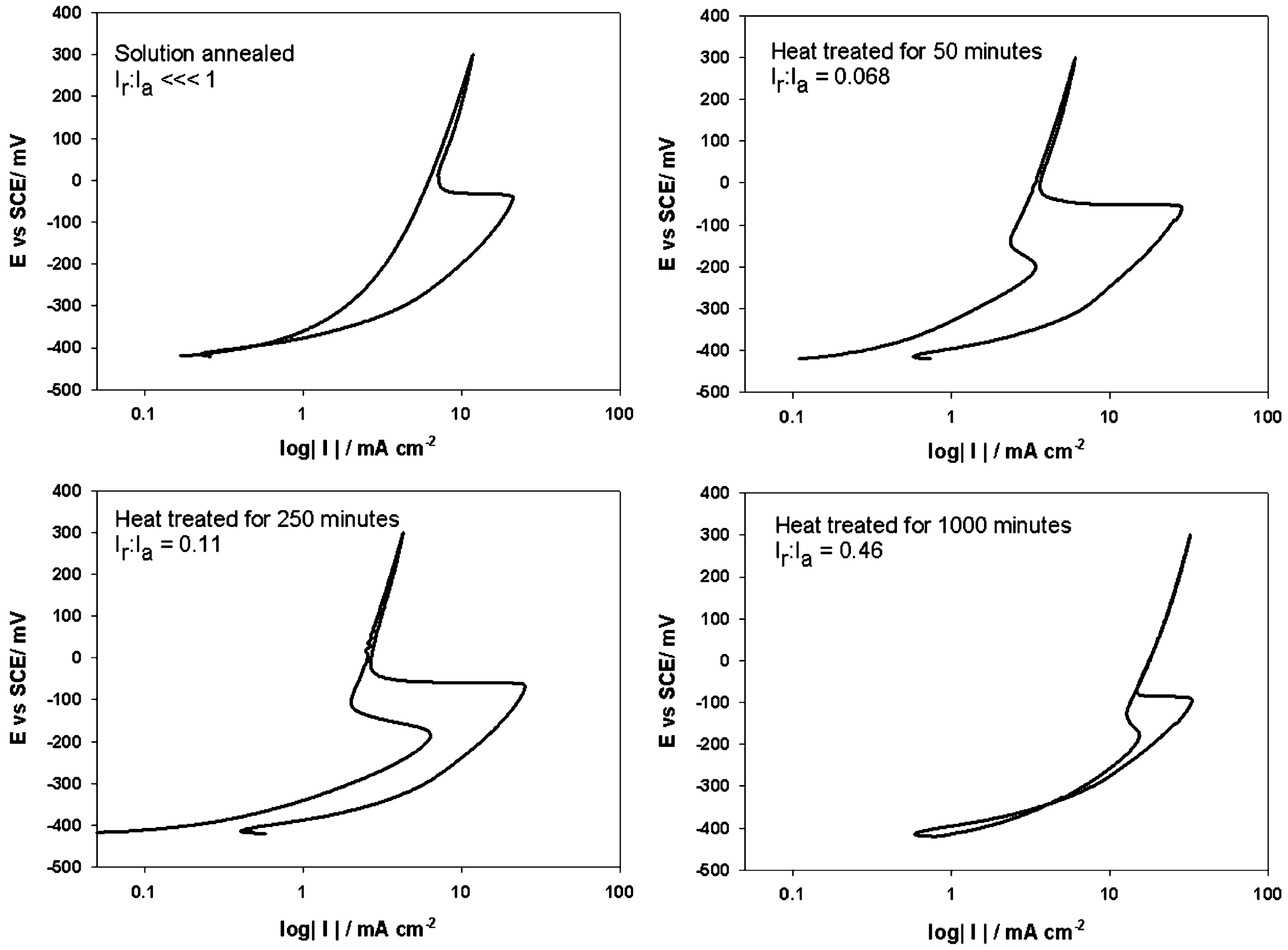

Fig. 3 DL EPR curves obtained from 304 SS samples subjected to different heat treatments

The principal aim of this work was to correlate the values of the RQA parameters obtained from the analysis of electrochemical current noise measurements with the sensitised condition of the 304 SS to assess the dynamics of the intergranular corrosion process. The data from the DLEPR tests provides the intensity of sensitisation as a function of the heat treatment time. It has been reported that intergranular corrosion of austenitic stainless steels in natural seawater is associated to high percentage of determinism [28]. On this basis, electrochemical noise measurements were conducted on samples subjected to heat treatment, after which solution annealed samples and specimens with different sensitisation intensities were induced.

3.3 Electrochemical noise tests

Figure 4 shows the current time series from electrochemical noise measurements of samples with different metallurgical conditions. The noise signal amplitude was increasingly higher as a function of the sensitisation intensity of the steel. The sensitised condition causes more periodic electrochemical current fluctuations. These fluctuations can be associated with intergranular corrosion to which sensitised stainless steels are susceptible specifically in the electrolyte used to conduct the tests [27, 29].

A remarkably attractive application of electrochemical noise technique is for identifying the type of corrosion, specifically localised corrosion. A number of parameters have been proposed as indicators of the extent of corrosion localisation such as the LI with which it was possible to avoid the problems associated with the expected value of zero for the mean current [30]. The LI values determined from the current time series clearly presented higher values for samples with higher sensitization intensity as shown in Fig. 5.

We found that this parameter displays a consistent relationship with the sensitization intensity, which may be evaluated by electrochemical current noise measurements. However, while the LI may by a useful meter of the nature of the corrosion process for specific metal-electrolyte systems, its sensitivity to the mean current and as a

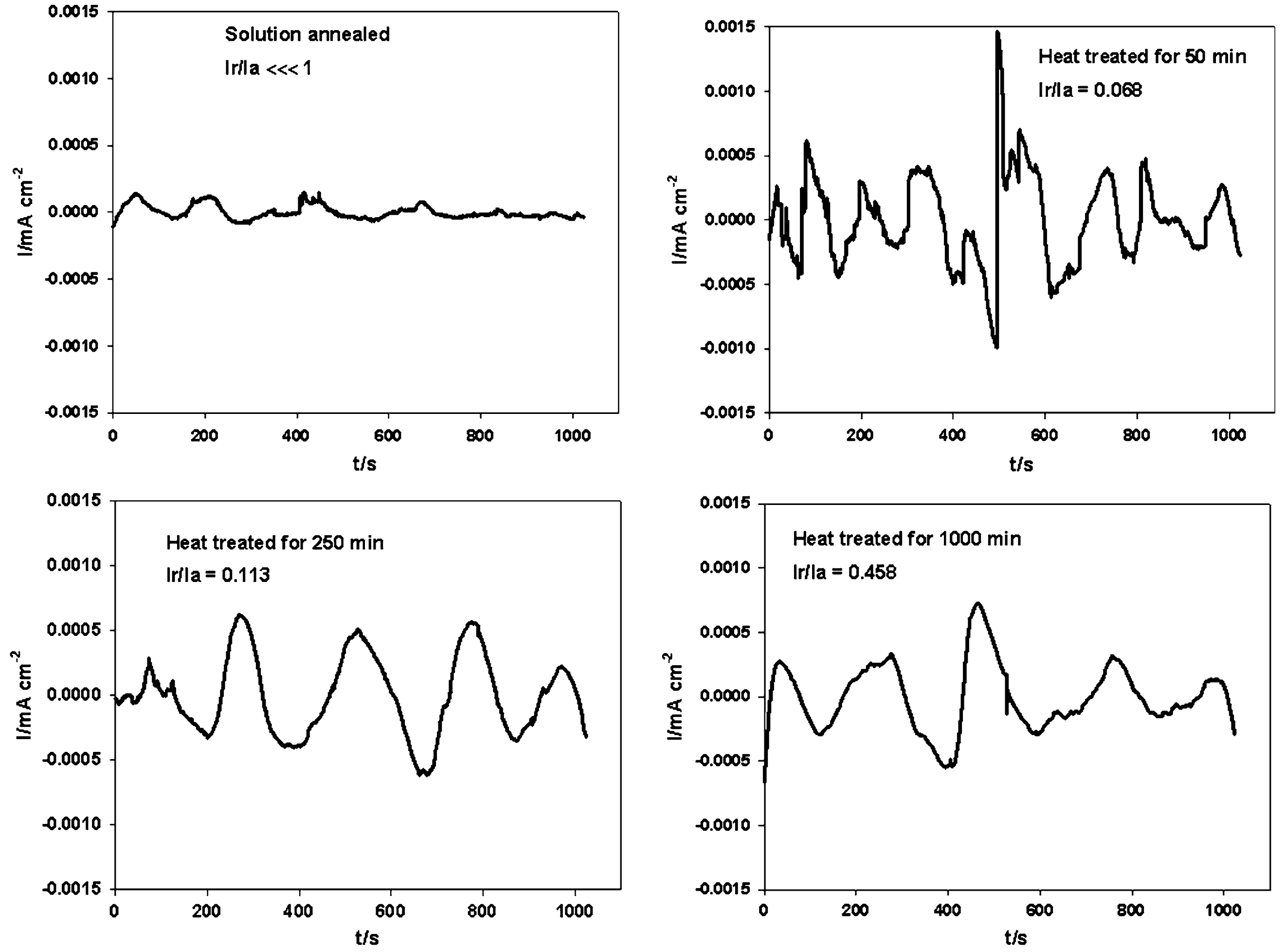

Fig. 4 Current time series for samples with different heat treatments

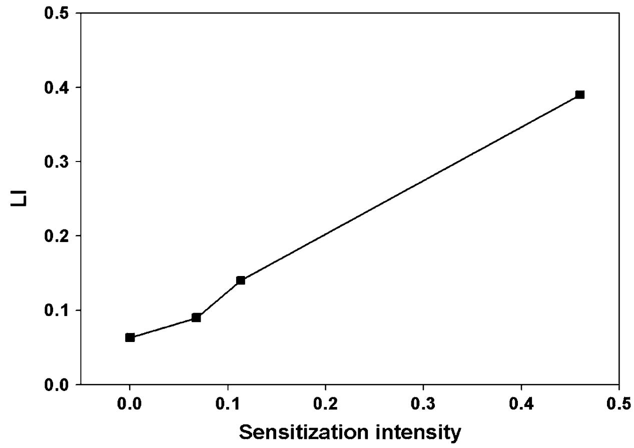

Fig. 5 LI as a function of the sensitisation intensity

consequence to any asymmetry between the two current-measuring electrodes, can lead to not consistent results. For the present case we will show next that the relationship between the LI and the sensitisation intensity was consistent as demonstrated by the results obtained from recursive plots analysis.

3.4 Recurrence plots analysis

Representative RPs obtained from the analysis of EN data of 304 SS samples with different intensities of sensitisation are shown in Fig. 6. A qualitative discussion of the recurrence characteristics of the system will be presented based on the RPs followed by a quantitative analysis based on the RQA parameters selected. All RPs presented in Fig. 6 are thresholded recursive plots and the points considered recurrent are classified into categories depending upon the magnitude of the distance and colour coded as follows: white and yellow pixels represent system states that are closest to each other in the reconstructed phase space, green pixels correspond to intermediate distances, while blue and black pixels represent still “recurrent states” but separated by even larger distances.

As can be observed, the sensitization condition of the SS samples modifies substantially the electrochemical noise

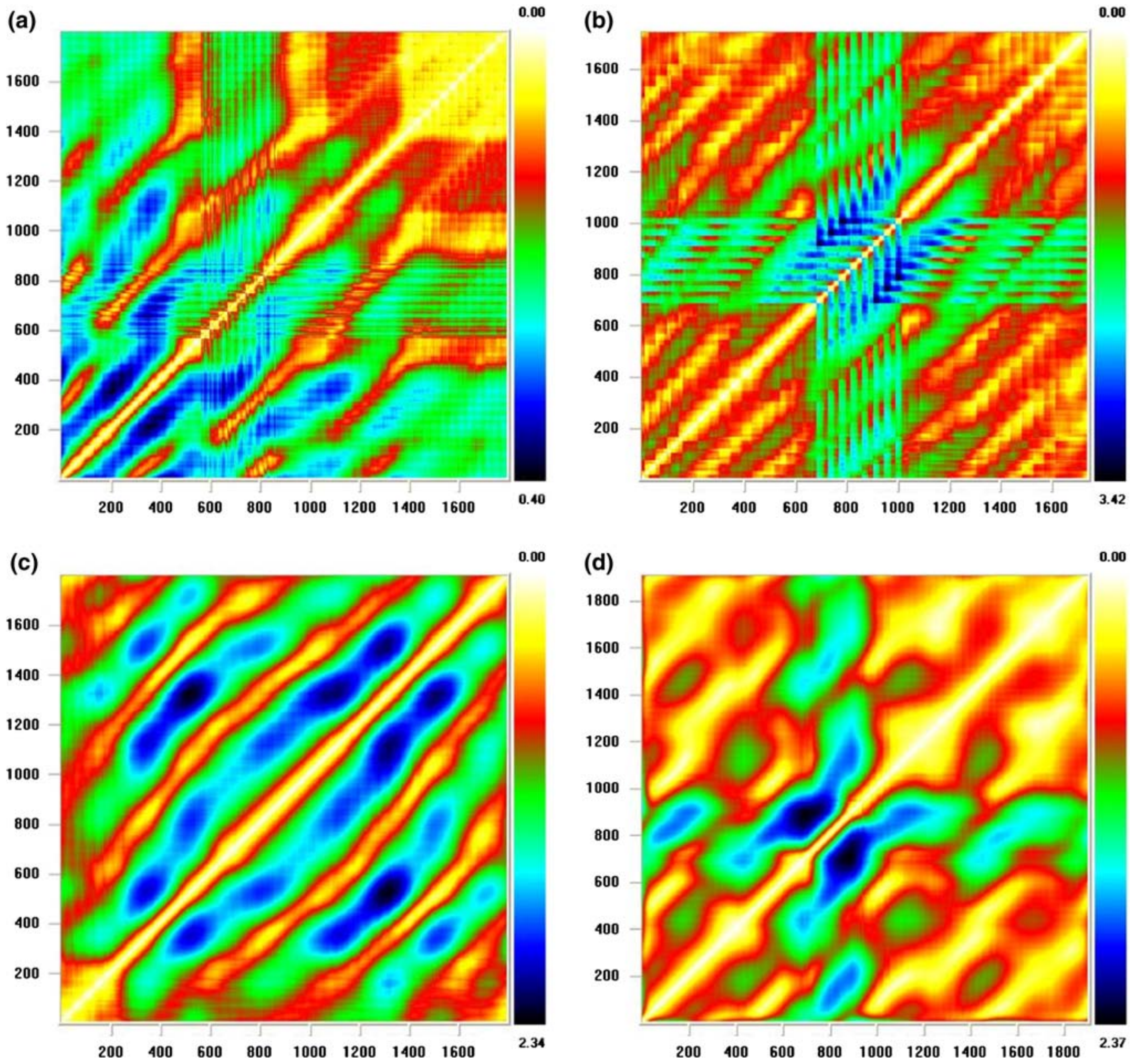

Fig. 6 Recursive plots obtained from samples with a sensitisation intensity of: A 0.00, B 0.068, C 0.46 and D 0.113

signal dynamics. This is clearly shown in the structure of the RP's where the number of points of short distances (white and yellow points) increment with the sensitization grade. This is an indication that the sites undergoing localised electrochemical activity in the SS develop an interaction between them inducing the dynamics of the process to a more deterministic or less chaotic state. This behaviour is observed in the RP's by the associated white and yellow points which formed large and more defined diagonal lines.

In order to go beyond the visual notion yielded by RPs, a number of measures of complexity which quantify the small scale structures in RPs, have been proposed [22, 24] and are known as recurrence quantification analysis (RQA).

In Fig. 7 we can see the tendency of the RQA parameters, specifically the percent recurrence (%R) and the percent determinism (%D) as a function of the sensitisation intensity.

As mentioned above, the percent recurrence (%R), quantifies the number of time instants characterized by a recurrence in the signals interaction: the more periodic the signal, the higher the %R value. The %R increased from a value of 1.96 when steel was not sensitized (SS in the as received condition and after solution annealing) to a value of 8.15 for the case of samples subjected to heat treatment

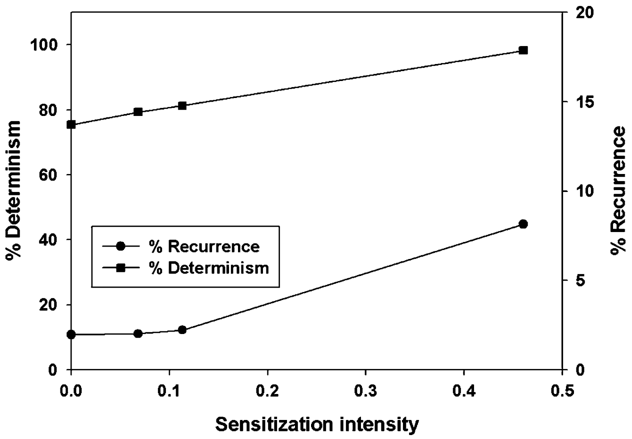

Fig. 7 %R and %D as a function of the sensitisation intensity

for 1,000 min at 923 K. This result along with the current time series indicates that as the sensitisation intensity increases the intergranular corrosion process presents a more periodic signal dynamics. This condition can be related to a dissolution process taking place at similar intensity in all sites susceptible to the intergranular attack. The chromium carbide precipitation induced an advantageous condition for localised corrosion to take place at the chromium depleted zones near the grain boundaries.

Periodic fluctuations of current can be associated to the presence of these chromium depleted zones near the grain boundaries that are preferential anodic sites on the metal surface which participate in a synchronised electrochemical interaction. From the electrochemical point of view this behaviour can be associated to the augmentation of non-passive surfaces as the sensitisation intensity increases. The presence of permanent (time and position), anodic sites during a dissolution process showed an electrochemical interaction between these sites as reported in the literature [31, 32].

The %D values also were higher as the sensitization intensity increased, ranging from 75.43 for samples subjected to solution annealing for which $I_r <<< I_a$ and as a consequence $I_r/I_a \rightarrow 0$ to 98.22 for samples aged 1,000 min at 923 K.

The high values of %D from 75% to 98% correspond physically to localised corrosion processes and the behaviour of this dynamical system as pointed out by Cazares-Ibañez et al. is quasi-periodic [33]. The high value of %D for the stainless steel in solubilised condition is associated to the effect of 0.5 M H_2SO_4 + 0.01 M KSCN solution which induce intergranular corrosion in the 304 SS. The ability of the electrolyte to promote intergranular attack is more evident on steel samples with larger sensitisation intensities.

In the present case the intergranular corrosion taking place in samples of sensitised steel in the specific electrolyte tends to present a stable interaction. The interaction between the sites undergoing localised corrosion (zones near the grain boundaries) induced a phenomenon of auto-organization reflecting in high values of %D [23, 24]. The intergranular corrosion process presented a more organized dynamics as the steel became more sensitised.

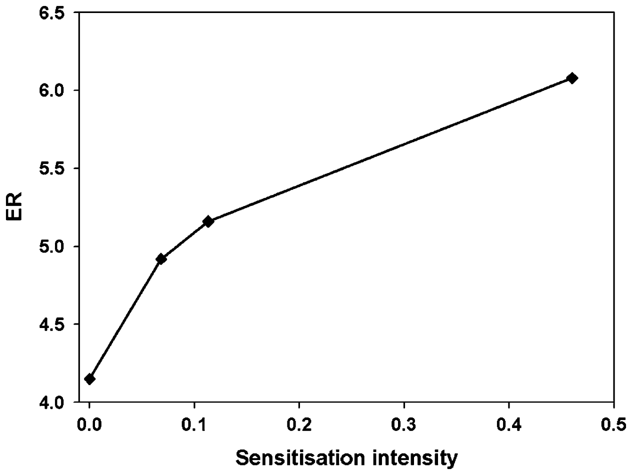

Fig. 8 Entropy recurrence as a function of the sensitisation intensity

Finally the ER values obtained increased as a function of the sensitization intensity as shown in Fig. 8. This indicates that independent of the degree of synchronization, the dynamics of the intergranular corrosion process became more complex as the sensitization intensity increased.

4 Conclusions

Electrochemical methods used to determine the sensitisation intensity on stainless steels enjoyed wide expansion over the last 40 years, and the DL-EPR test has become one of the most successful due to its quantitative and quasi-non destructive nature. However as with any testing technique, attention must be paid in interpreting the results as measurements are sensitive to local changes in composition and microstructure of the alloy under study.

A novel analysis method for processes with non-linear dynamics was presented in this paper. The analysis of electrochemical current noise measurements, which had the advantage of being a non-intrusive technique, detected different sensitisation intensities on S30400. Current time series showed higher amplitude and a more periodic pattern as the sensitisation intensity was larger. According to this response, the LI showed higher values for samples with larger sensitisation intensities indicating that the corrosion process tended to be more localised.

The analysis of electrochemical noise in current using the novel methodology of recurrence plots proved to be an excellent tool to evaluate the changes in the dynamics of the corrosion process in S30400 SS with different sensitization intensities in 0.5 M $H_2SO_4 + 0.01$ M KSCN.

The RQA of the RP's showed that sensitisation causes a localised corrosion process with spatiotemporal well defined electrochemical cells interacting in the form of a dissolution process with periodic dynamics. The periodicity was determined by the increment of %D and R% as a function of the sensitisation intensity. This interaction becomes more complex when increasing the sensitization condition as indicated by the ER increasing values.

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References

1. Lacombe P, Baroux B, Beranger G (1993) Stainless steels. Les editions de physique, France
2. Sedriks AJ (1996) Corrosion of stainless steels, 2nd edn. Wiley, USA
3. Marshall P (1984) Austenitic stainless steels, microstructure and mechanical properties. Elsevier, England
4. Terada M, Saiki M, Costa I, Fernando A (2006) J Nucl Mater 358:40
5. Shaikh H, Sivaibharasi N, Sasi B, Anita T et al (2006) Corros Sci 48:1462
6. Číhal V, Štefec R (2001) Electrochim Acta 46:3867
7. Novak P, Štefec R, Franz F (1975) Corrosion 31:344
8. Standard G 108–94 (1994) Annual book of ASTM standards 1995. American Society for Testing and Materials, Philadelphia, PA, p 444
9. Majidi AP, Streicher MA (1984) Corrosion 40:584
10. Zaveri N, Sunb R, Zufelt N, Zhoua A, Chenb YQ (2007) Electrochim Acta 52:5795
11. Cottis R, Turgoose S (1999) Electrochemical impedance and noise. NACE, Houston, TX
12. Gouveia-Caridade C, Pereira IM, Brett MA (2004) Electrochim Acta 49:785
13. García-Ochoa E, Hernández MA, Rodríguez FJ, Genescá J, Boerio FJ (2003) Corrosion 59:50
14. Markworth AJ, Stringer J, Rollins RW (1995) MRS Bull 20:20
15. Li Z, Cai J, Zhou S (1997) J Electroanal Chem 432:111
16. Karantonis A, Pagitsas M, Miyakita Y, Nakabaya S (2005) Electrochim Acta 50:5056
17. Parmananda P, Rivera M, Green BJ, Hudson JL (2005) Appl Math Comput 164:467
18. Zhai Y, Kiss IZ, Daido H, Hudson JL (2005) Physica D 205:57
19. Eckmann JP, Kamphorst SO, Ruelle D (1987) Europhys Lett 4:973
20. Casdagli MC (1997) Physica D 108:12
21. Trulla LL, Giuliani A, Zbilut JP, Webber CL (1996) Phys Lett A 223:255
22. Zbilut JP, Webber CL (1992) Phys Lett A 171:199
23. McGuire G, Azar NB, Shelhamer M (1997) Phys Lett A 237:43
24. Webber CL Jr, Zbilut JP (1994) J Appl Physiol 76965:973
25. Alvarez CJ, Almanza E, Murr LE (2005) J Mater Sci 40:2965
26. Lima AS, Am Nascimento, Abreu HF, De Lima Neto P (2005) J Mater Sci 40:139
27. Was GS, Rajan VB (1987) Corrosion 43:576
28. Acuña N, García-Ochoa E, González-Sánchez J (2008) Int J Fatigue 30:1211
29. Amadou T, Braham C, Sidhom H (2004) Metall Mater Trans A 35A:3499
30. Cottis R (2001) Corrosion 57:265
31. Wu B, Scully JR, Hudson JL, Mikhailov AS (1997) J Electrochem Soc 144:1614
32. Kiss I, Wang W, Hudson JL (2000) Phys Chem Chem Phys 2:3847
33. Cazares-Ibáñez E, Vázquez-Coutiño GA, García-Ochoa E (2005) J Electroanal Chem 583:17