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Pitting corrosion of stainless steel by electrochemical noise technique

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Abstract
Electrochemical noise (EN) corrosion monitoring technique has become an interesting method in corrosion measurement systems. Detection and analysis of early stages of localized corrosion is the best advantage of this testing technique. Signal analyses and understanding the obtained current and potential transients are limited. In this work, the pitting corrosion behavior of 304 and 316 stainless steel in ferric chloride solution was investigated by electrochemical noise measurement technique. Results obtained from current and potential transients were in correlation with surface analysis performed by scanning electron microscopy. Tests were conducted at three different temperatures, 40, 50, and 60°C. Results showed that 304 stainless steel exhibited general corrosion associated with pitting corrosion, this effect increased as temperature increased. 316 stainless steel showed only pitting corrosion with no general corrosion, the effect of temperature on 316 was less.

Keywords: Electrochemical noise, pitting, stainless steel.

Introduction
Electrochemical noise is the fluctuation in electrode potential and current in some electrochemical environment. Electrochemical noise analysis is a unique technique in electrochemical corrosion analysis, and this is because it can be performed for open circuit conditions, does not need external perturbations of the system, and, the spontaneous changes in current and voltages are sufficiently small. Electrochemical noise data acquisition requires simple experimental setup compared with in situ testing.
First studies of electrochemical noise focused on the relation between potential, current, and corrosion rate (1-3). These approaches were suitable in localized corrosion studies, such as stress corrosion cracking and pitting. However, qualitative information can be given by potential or current monitoring. Later studies were directed for monitoring the potential and coupling current from two coupled identical electrodes (4-11). Quantitative corrosion rate studies can be made according to these studies. Noise resistance (Rn), which is the ratio of the standard deviations of the potential noise (σ_E) and coupling current change (σ_1) is the most important step in this method:

$$\mathbf{Rn = (\sigma_E / \sigma_1)} \qquad \textbf{(1)}$$

Chen and Skerry (8) and Eden et al. (6) suggested that Rn should be related to the polarization resistance (Rp) that was commonly determined by linear polarization techniques or electrochemical impedance spectroscopy (EIS).
The aim of this work is to study the effect of temperature on corrosion behaviour of 304 and 316 stainless steel in 0.6 M ferric chloride solution.

2. Materials and methods
Series of identical electrodes made of stainless steel sheets of S30400 and S31600 stainless steel electrodes are used to evaluate pitting corrosion in high chloride solution. Chemical composition of stainless steel sheets used is given in Table 1.

Table1: Chemical composition of stainless steel sheets.

	C	Cr	Ni	Mn	Si	S	P	Mo
SS304	0.14	18	10	2.1	1.0	0.03	0.04	-
SS316	0.07	17	10	2.0	1.0	0.03	0.04	2.2

Samples were cut to 2mm x 7mm x 7mm size, soldered to a copper wire and embedded into epoxy resin ground to 1000 grit using emery papers, proper chemical cleaning by acetone was performed to specimen surface. The exposure area of samples was 0.5 cm^2. Ferric chloride solution was prepared and used as the testing solution. Three-electrode

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electrochemical cell system [12, 13] (two identical working electrodes 1 and 2, and a reference electrode) saturated calomel electrode was used as the reference electrode; the two identical electrodes were connected to ZRA (zero resistance ammeter) [14, 15], the experimental setup is shown in Figure1.

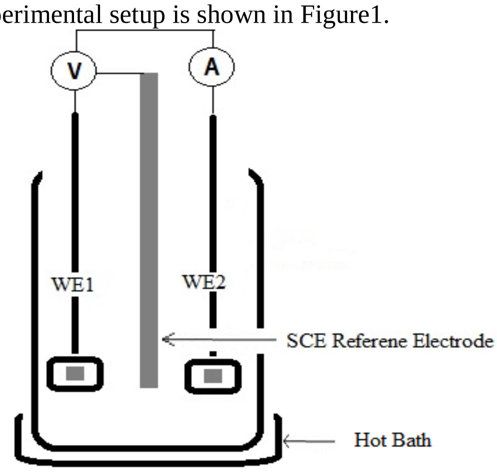

Figure1: Three-electrode cell experimental setup.

Electrochemical current and potential noises of 304 and 316 stainless steel specimens were simultaneously in 0.6M ferric chloride solution, all noise measurements were performed at 40^0 C, 50^0 C, and 60^0 C temperatures**.**

3. Results and discussion

The influence of temperature on both 304 and 316 stainless steel samples tested in 0.6 M ferric chloride solution is shown in Figures (2-9).

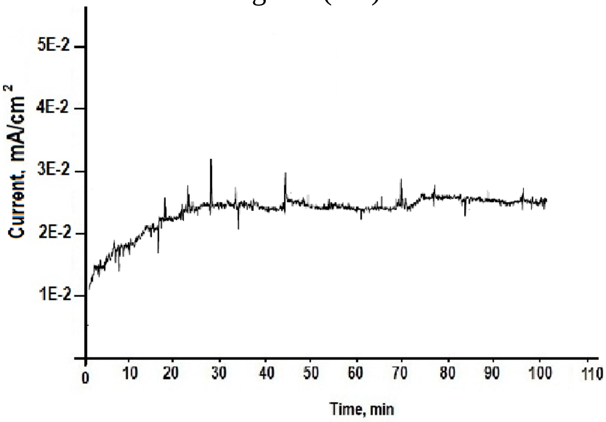

Figure 2: Current time series of 304 stainless steel tested in 0.6M ferric chloride solution at 40^0C.

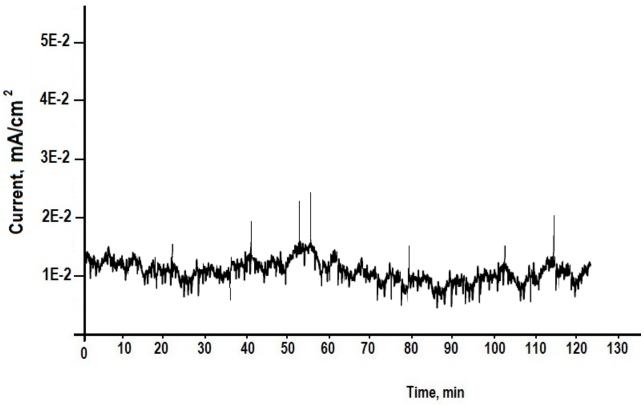

Figure 3: Current time series of 304 stainless steel tested in 0.6M ferric chloride solution at 50^0C.

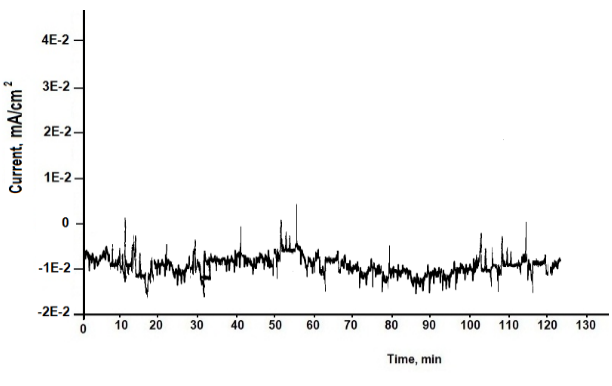

Figure 4: Current time series of 304 stainless steel tested in 0.6M ferric chloride solution at 60^0C.

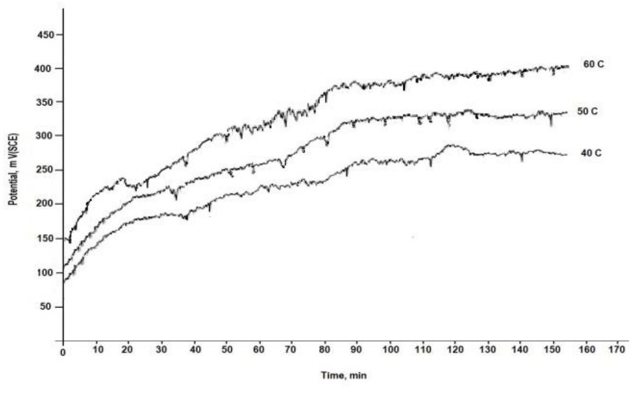

Figure 5: Potential time series of 304 stainless steel tested in 0.6M ferric chloride solution.

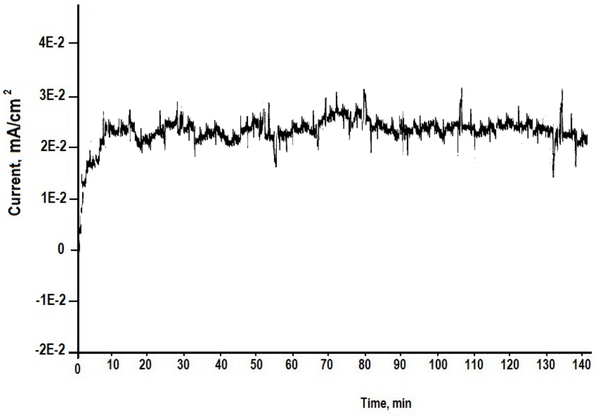

Figure 6: Current time series of 316 stainless steel tested in 0.6M ferric chloride solution at 40^0C.

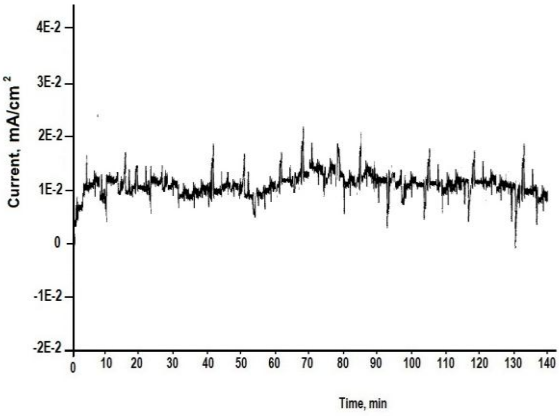

Figure 7: Current time series of 316 stainless steel tested in 0.6M ferric chloride solution at 50^0C.

Figures (2-5) showing the potential and current transients of 304 stainless steel specimens which were simultaneously measured as a function of time using zero resistance ammeter (ZRA), in 0.6 M ferric chloride solution at 40^0C, 50^0C, and 60^0 C. Fluctuations in potential and current transients with some passivity are shown for samples tested at 40^0C (Figures 2 and 5), fluctuations in current increased with higher amplitudes and a shift in potential to the active direction was noticed for those samples tested at higher temperatures 50^0C, and 60^0C (Figure 3, Figure4, and Figure 5). Fluctuations in potential and current are considered to be associated with passive film breakdown and metastable pits initiation. A deep metastable pit can form a stable pit because of the corrosive solution that prevents re-passivation (16). Sato (17) suggested that the corrosion potential of passive metal decreases as a metastable pit grows entering the active state as a stable localized corrosion. Small fluctuations in current and potential transients for 316 stainless steel samples were noticed at all testing temperatures leading to less pit initiation and less passive to active state transition (18-22). Figure 6 shows the recorded current time series of UNS316 stainless steel tested at 40^0 C, some transients were observed in both directions, these transients are associated to localized corrosion; pitting. Figures 7 and 8 show the current time series of 316 grade stainless steel tested at 50^0 C and 60^0 C respectively, in both Figures there are transients recorded in both sides, transients being similar for the three testing temperatures, these transients were revealing to pitting occurring on stainless steel surface. Potential time series of 316 stainless steel tested at all temperatures (40^0C, 50^0C, 60^0C) is shown in Figure 9. Small fluctuations in transients are shown compared to UNS304 grade stainless steel. The effect of temperature on this type of stainless steel being less compared to 304, this is shown in current and potential transients.

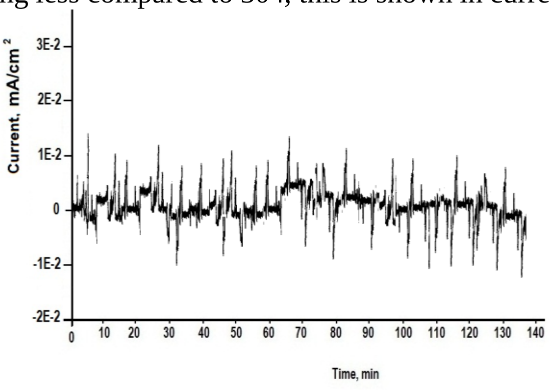

Figure 8: Current time series of 316 stainless steel tested in 0.6M ferric chloride solution at 60^0C.

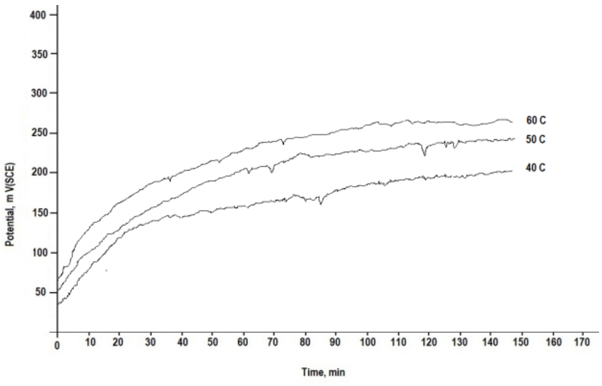

Figure 9: Potential time series of 316 stainless steel tested in 0.6M ferric chloride solution.

The scanning electron micrographs of stainless steel surfaces are in agreement with electrochemical noise measurements obtained. Figures (10-12) show the SEM micrograph of 304 stainless steel tested at all testing temperatures, pitting with general corrosion are seen as an etching effect of surfaces, the microstructure is being developed due to etching effect. 316 stainless steel showed only pitting behaviour with no general corrosion (etching effect) this is shown in Figures (13-15). Discussion is very poor and merits to be developed adequately and insert Figs in corresponding part.

Figure 10: SEM micrograph of 304 stainless steel tested at 40^0C, 100x.

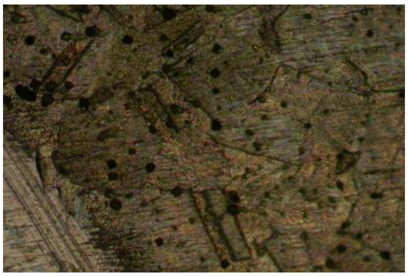

Figure 11: SEM micrograph of 304 stainless steel tested at 50^0C, 100x.

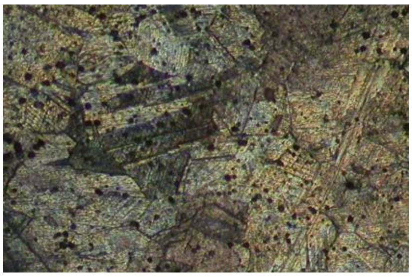

Figure 12: SEM micrograph of 304 stainless steel tested at 60^0C, 100x.

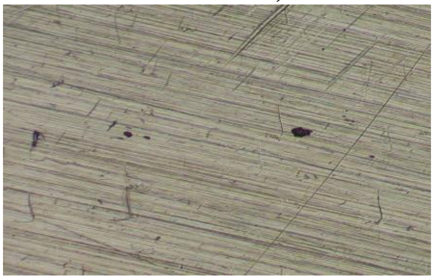

Figure 13: SEM micrograph of 316 stainless steel tested at 40^0C, 100x.

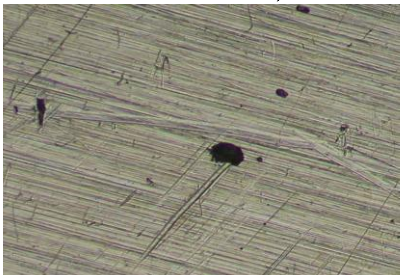

Figure 14: SEM micrograph of 316 stainless steel tested at 50^0C, 100x.

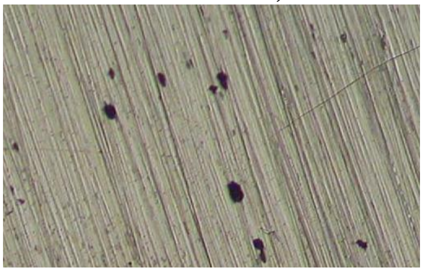

Figure 15: SEM micrograph of 316 stainless steel tested at 60^0C, 100x.

Conclusion

1- Electrochemical noise measurements showed double effect of ferric chloride solution on 304 stainless steel at all temperatures.
2- Current and potential transients increased with temperature revealing pitting and general corrosion effect on 304.
3- General corrosion on 304 was in the form of etching due to etching effect of ferric chloride solution on stainless steel.
4- Current and potential noise transients were less in 316 stainless steel at all temperatures compared to 304.
5- The effect of testing solution on 316 stainless steel was as pitting corrosion with no noticeable general corrosion.
6- The effect of testing temperature on 316 was negligible.

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