

ELECTROCHEMICAL NOISE MEASUREMENTS FOR CHARACTERIZATION OF PATINA RUST ON WEATHERING STEEL

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Abstract

Electrochemical noise analysis (ENA) was used for the evaluation of corrosion protective properties of patina rust layer formed on weathering steel S355J23W after 8 years of exposure test in Berlin atmosphere. Electrochemical parameters derived from shot noise theory were obtained and related with changes or degradation in tested rust film during 456 h exposure in SO₄²⁻ and Cl⁻ containing aqueous solution. The electrochemical data was compared with other standard corrosion data.

Keywords: Weathering steel, corrosion loss, protective patina, electrochemical noise

1. INTRODUCTION

In spite of an overwhelming evidence as far as the efficiency of low alloying in slowing down the atmospheric attack [1, 2], very low attention was paid to possible application of electrochemical measurements on rusted specimens of low alloy steels. In fact it was firstly the work at Rome [3] which has shown that e.g. corrosion potential and polarization measurements performed in 0.1 M Na₂SO₄ on rusted specimens of this type of steels can be used as emphasizing either effect of the additions on certain physico-chemical properties of the rust or their influence on the electrode behavior of steel. Unfortunately any other works on development of potential sweep techniques on rusted specimens have not been performed in 0.1M Na₂SO₄. One of possible reasons of this can be the fact that potential sweep techniques are generally considered as destructive for rusted specimens.

In this paper, we demonstrate the possibility to follow the sequence of degradation events in patina rust on low alloy steel (which had been exposed to given type of atmosphere for the desired time and then immersed in modified version of 0.1 M Na₂SO₄ solution by means of electrochemical noise analysis (ENA). Although there is no established procedure based on ENA applications for study of protective properties of patina on weathering steel, ENA is generally accepted as a non - destructive/non - intrusive technique making possible monitoring of basic changes in an electrochemically active systems. For these reasons we tested this method for monitoring degradation or changes in protective properties of rust film formed by weathering of steel S355J23W when it was immersed in 0.1 M Na₂SO₄ + 0.001 M NaCl. For this solution it was expected that ENA measurements can be sensitive to changes in initially protective character of tested patina rust layer if wetting period (immersion time in test solution) is excessive.

2. EXPERIMENTAL

Test specimen used in this work were small segments cut of weathering steel S355J2W (see chemical composition in **Table 1**) with patina layer covering the whole surface of specimens. Total thickness of this patina layer (formed during 8 years of exposure of the mentioned steel to Berlin atmosphere) was 120 μm

Table 1 Chemical composition of weathering steel S355J2W (wt. %)

C	Mn	Si	P	S	Cr	Ni	Cu	Mo	V	Al	Ti	N
0.146	1.400	0.360	0.020	0.010	0.500	0.030	0.300	0.005	0.040	0.0033	0.003	0.006

Two identical specimens with the same area of rusted surface (0.382 cm²) exposed to 0.1 M Na₂SO₄ + 0.001 M NaCl solution were used as separate working electrodes. All measurements were performed in special cell manufactured for EN measurements in SVUOM Ltd. The details and the description of the cell can be found elsewhere [4]. As reference electrode was used silver/silver chloride electrode (SSCE) and the potential and current noise (ENP and ENC) values for given data set were measured at different exposure times. Due to uninterrupted immersion test under conditions indicated above EN signals were recorded on patina electrodes using zero - resistance ammetry in open circuit, a procedure believed to be capable monitoring changes of corrosion potential at electrochemically active the steel/patina interface as well as noise characteristics from the anodic and cathodic reactions occurring on anodic and cathodic sites of patina rust layer. In presented work all ENP as well as ENC signals were collected in measurements periods of 600 s with sampling frequency of 20 Hz using GAMRY potentiostat with ESA 410 software. Data treatment in both time (E_{mean} values) and frequency domain was used with the aim to verify if by means of this test procedure selective evaluation of patina rust degradation on experimental steel after long duration atmospheric exposure could be possible. For this purpose Fast Fourier Transform (FFT) was used for transforming EN time records to the frequency domain where low frequency values of power spectral densities of potential and current (PSD_E and PSD_I) for given bandwidth of EN measurements were estimated. It should be notice these values PSD_E and PSD_I (0.15 Hz) can be related to shot noise parameter q if shot noise theory is applied to EN [5]. In fact q is an indication of the mass of metal lost in the event and for given system could be calculated according to the equation

$$q = \frac{\sqrt{PSD_E} \sqrt{PSD_I} (0.15\text{Hz})}{B} \quad (1)$$

only if values B (Stern-Geary constant) is known.

As B can be assumed to be equal for all EN measurements performed in given system it should not to be considered for monitoring changes or degradation in tested rust film. For this purpose we used a new parameter, so called statistical noise power (P_n) represented by equation

$$P_n = \sqrt{PSD_E} \sqrt{PSD_I} (0.15\text{Hz}) \quad (2)$$

3. RESULTS AND DISCUSSION

It is believed that a good behavior of patina rust layer (formed on low alloyed steel after long duration of atmospheric performance) can be attributed to a layer of α -FeOOH [6]. This layer is formed if the electrode potential at rust/steel interface is sufficiently high for Cu and other alloying elements to pass into the rust and catalyze the conversion of γ -FeOOH into protective α -FeOOH. If this type of protective patina rust/steel interface is exposed to 0.1 M Na₂SO₄ + 0.001 M NaCl solution it can be expected that the electrode potential at rust/steel interface is changing with time. In situation when with increasing time of exposure the potential at rust/steel interface is too low for Cu and other elements to pass into rust, non-protective magnetite is formed and the rust does not prevent corrosion. In open air conditions of test solution the magnetite formed cathodically can be quickly oxidised by air to give fresh ferric rust on patina rust layer. According to it is obvious from **Figure 1** (where E_{mean} value is used for the electrode potential at rust/steel interface) that protective character of patina rust layer exposed to test solution can be preserved for not only to excessive wetting period (time of exposure to test solution). It can be expected differences for tested patina layer should also be confirmed by low frequency values of PSD_E and PSD_I (0.15 Hz) estimated for different times of exposure of given system to test solution (see **Table 2**). When using these values for calculations of P_n values, time development of state of degradation for tested patina rust layer according to mechanism mentioned above can be depicted (see **Figure 1**).

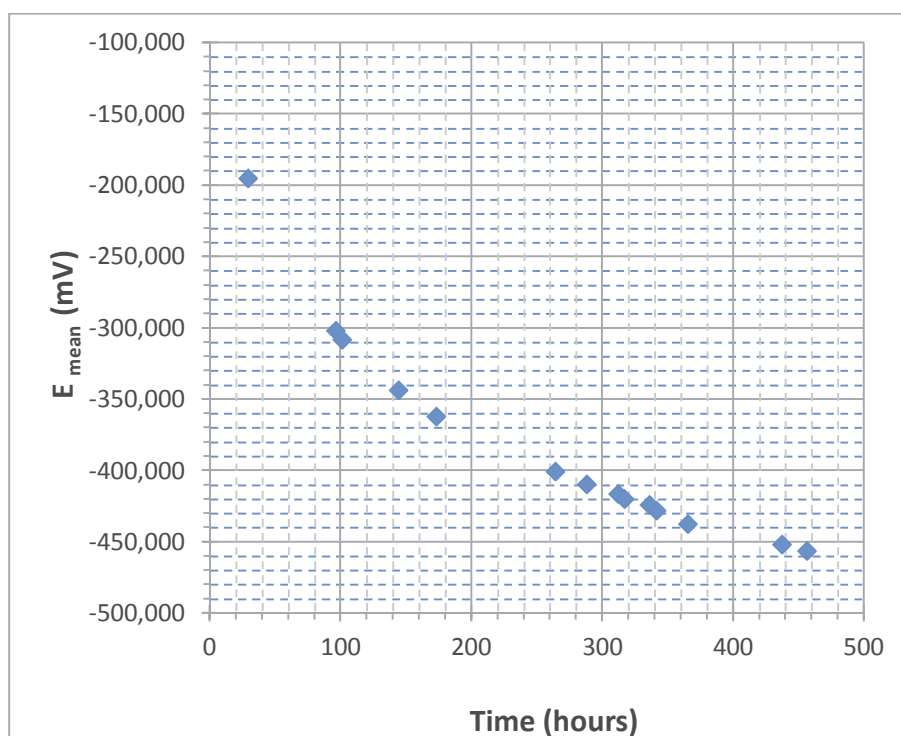


Figure 1 Evaluation of E_{mean} (vs. SSCE) development with immersion time for patina rust during exposure in 0.1 M Na_2SO_4 + 0.001 M NaCl solution

Table 2 Low frequency values of PSD_E and PSD_I (0.15 Hz) for given bandwidth EN measurements estimated from EN measurements performed at different times of exposure of tested patina rust

Exposure time (hrs)	PSD_E ($\text{V}^2 \cdot \text{Hz}^{-1}$)	PSD_I ($\text{A}^2 \cdot \text{Hz}^{-1}$)
29	$1.85 \cdot 10^{-5}$	$2.20 \cdot 10^{-14}$
96	$4.40 \cdot 10^{-5}$	$1.02 \cdot 10^{-14}$
101	$4.70 \cdot 10^{-5}$	$1.05 \cdot 10^{-14}$
144	$5.80 \cdot 10^{-5}$	$1.05 \cdot 10^{-14}$
173	$6.70 \cdot 10^{-5}$	$1.00 \cdot 10^{-14}$
264	$8.00 \cdot 10^{-5}$	$1.72 \cdot 10^{-14}$
288	$8.05 \cdot 10^{-5}$	$2.45 \cdot 10^{-14}$
312	$8.35 \cdot 10^{-5}$	$3.50 \cdot 10^{-14}$
317	$8.70 \cdot 10^{-5}$	$3.83 \cdot 10^{-14}$
336	$8.70 \cdot 10^{-5}$	$4.45 \cdot 10^{-14}$
341	$9.00 \cdot 10^{-5}$	$4.60 \cdot 10^{-14}$
365	$9.10 \cdot 10^{-5}$	$5.85 \cdot 10^{-14}$
437	$1.01 \cdot 10^{-4}$	$1.00 \cdot 10^{-13}$
456	$1.01 \cdot 10^{-4}$	$1.32 \cdot 10^{-13}$

Based on the above findings, the cross-sectional observations of patina rust film for non-exposed and exposed surface has been performed (see **Figure 2 - 4**). The expected features of corrosion resistant patina can be seen from **Figure 3** as well as anomalous rust formation after 456 hrs exposure in 0.1 M Na_2SO_4 + 0.001 M NaCl solution from **Figure 4**.

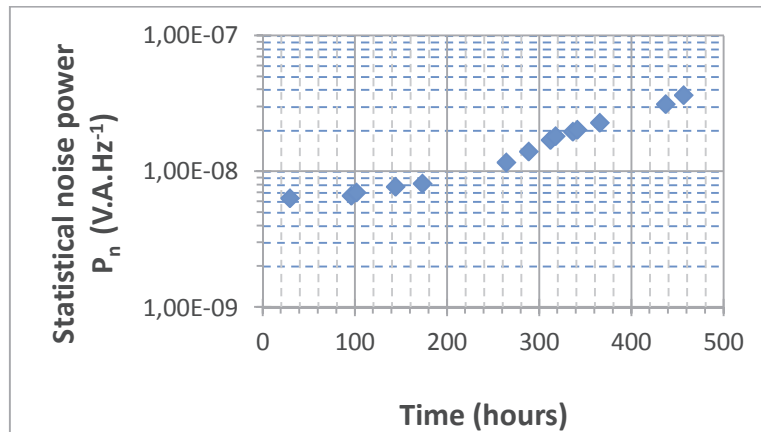


Figure 2 Time development of state of degradation by means of P_n values estimated for tested patina rust during exposure in 0.1 M Na_2SO_4 + 0.001 M NaCl solution

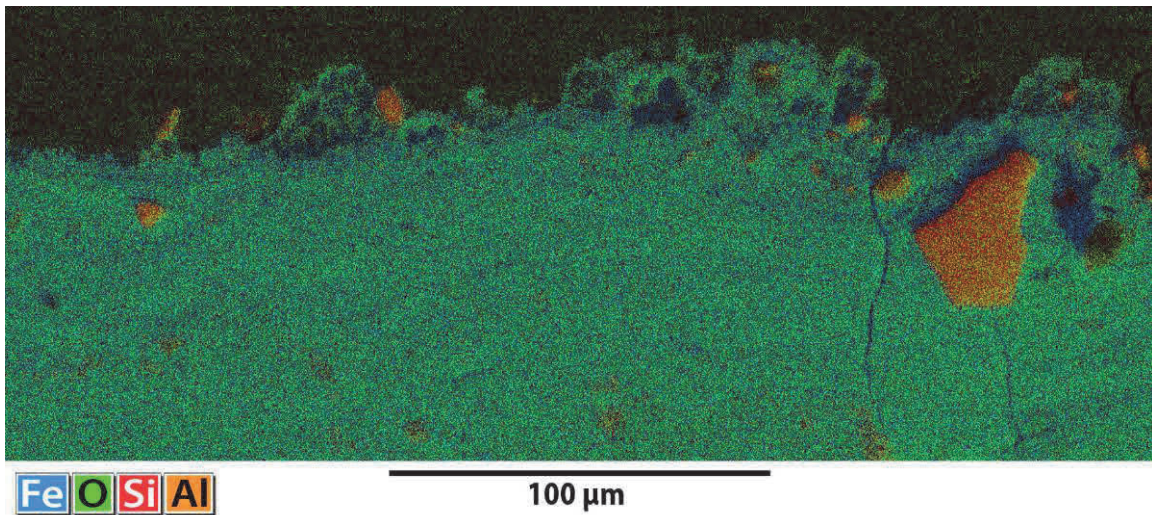


Figure 3 EDX mapping and structure (SEM-ES image) - cross-section of patina rust layer non-exposed to 0.1 M Na_2SO_4 + 0.001 M NaCl solution

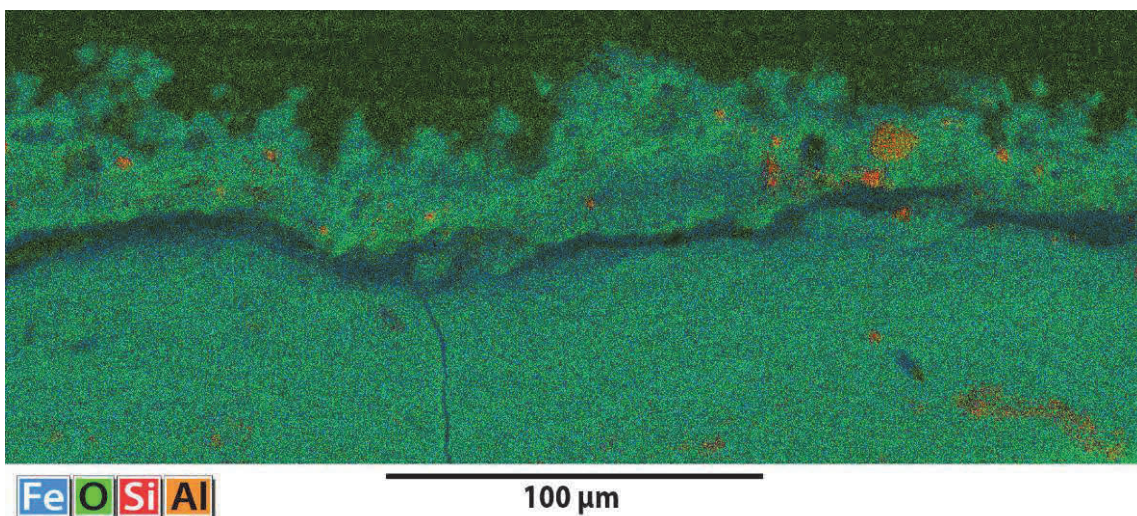


Figure 4 EDX mapping and structure (SEM-ES image) - cross-section of patina rust layer after 456 hrs of exposure to 0.1 M Na_2SO_4 + 0.001 M NaCl solution

4. CONCLUSION

The results obtained from the metallographic evaluation have been compared with electrochemical parameters estimated from EN measurements relating to evaluation of patina rust on experimental steel after long duration of atmospheric performance. Possible interpretation was found and reasonably good correlation observed between metallographic evaluation and parameters estimated from EN measurements. Although further investigation is necessary, the obtained results suggest that EN could be used as selective evaluation of patina rust on experimental steels after long duration of atmospheric performance.

ACKNOWLEDGEMENTS

The article was written with support of project MPO - IP 9/2017.

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