Using Thionates for Noise Experiments – a Reasonable Combination?

Thionate und Rauschexperimente – eine geeignete Kombination?

S. Ritter*, T. Dorsch and R. Kilian

The detection of intergranular corrosion (IGC) initiation of austenitic stainless steel (AISI 347) coupon specimens was investigated using electrochemical noise (EN) measurements. The tests were performed in acidic sodium tetrathionate ($\text{Na}_2\text{S}_4\text{O}_6$) solution. The IGC initiation in tetrathionate solution could not be clearly detected by the electrochemical potential noise signal due to interferences of the noise signal with chemical processes which occurred in the test solution. This was confirmed by tests with inert platinum specimens. It was concluded that EN results obtained by tests in thionate or comparable sulfur containing solutions should be regarded with great care and verified, e.g., by tests with inert specimens.

Keywords: Electrochemical noise, intergranular corrosion, thionate, sulfur, austenitic stainless steel.

Die Detektion der Initiierung interkristalliner Korrosion im austenitischen Stahl der Werkstoffnummer 1.4550 (AISI 347) wurde mit elektrochemischen Rauschmessungen untersucht. Die Versuche wurden in saurer Natriumtetrathionatlösung ($\text{Na}_2\text{S}_4\text{O}_6$) durchgeführt. Durch die Wechselwirkung des Rauschsignals mit chemischen Reaktionen der Versuchslösung konnte die Initiierung von interkristalliner Korrosion nicht eindeutig durch das Potentialrauschen detektiert werden. Dies wurde durch Versuche mit inerten Platinproben bestätigt. Daraus wurde gefolgert, dass Ergebnisse aus elektrochemischen Rauschmessungen in thionathaltigen oder vergleichbaren schwefelhaltigen Lösungen mit grosser Sorgfalt betrachtet und z.B. durch Versuche mit inerten Proben überprüft werden sollten.

Reproduced with permission from NACE International, Houston, TX, USA. All rights reserved. Paper 04458 presented at CORROSION/2004, New Orleans, LA, USA. © NACE International 2004.

Stefan Ritter: Paul Scherrer Institute (PSI)
Nuclear Energy and Safety Research Department
Laboratory for Materials Behaviour
CH-5232 Villigen PSI, SWITZERLAND
e-mail: stefan.ritter@psi.ch, Tel.: +41 56 310 2983, Fax: +41 56 310 2199

Thomas Dorsch, Renate Kilian:
Framatome ANP GmbH, NGTM
Freyeslebenstr. 1, D-91058 Erlangen, GERMANY

1 Introduction

More than 35 years ago Iverson was one of the first who performed electrochemical noise (EN) measurements during corrosion processes [1]. With help of a loudspeaker he detected potential fluctuations, caused by metal dissolution of an iron specimen in acidic hexacyanoferrate solution [2]. At the same time Tyagai investigated the EN behavior of redox reactions of iron ferrite/ferrate and iodite/iodate with platinum and cadmium sulfide electrodes [3 – 6]. Nevertheless, only from the year 1983 on an increasing number of publications in the area of EN was registered. In the early 90`s the first commercial EN measurement devices for monitoring corrosion in the field were available [7]. This slow development is mainly due to the seemingly random and irreproducible results and the low performance of computer technology in these days. The fast development of the computer equipment made the production of EN measurement devices and also the recording and evaluation of the noise data much easier. Nevertheless the measurement and evaluation of EN in terms of the detection of corrosion processes still seems to be a challenge in some corrosion systems, although more and more the EN has emerged from the research laboratory and found applications in operating plants as versatile corrosion monitoring and measurement technique [8].

EN is defined as fluctuations of potential or current, typically of low frequency (< 10 Hz) and low amplitude. EN originates, in part, from natural variations in electrochemical kinetics during a corrosion process. EN is often regarded as a random (stochastic) phenomenon coupled to deterministic kinetics [9]. Numerous investigations of experienced scientists revealed a dependence of the frequency or intensity of the potential and current fluctuations on the material, potential, temperature and electrolyte, thus on the corrosion mechanism [9 – 13]. Furthermore the EN technique has the potential to detect nucleation and initiation of corrosion processes [8]. Some of the major sources of noise observed in electrochemistry and corrosion are:

- motion of ions adjacent to the electrode surface,
- gas bubble nucleation, growth and detachment from the electrode surface,
- mass transport to the corroding surface,
- changes of the electrolyte resistance adjacent to the corroding electrode caused by concentration gradients,
- local temperature gradients, and
- corrosion processes (e.g., initiation/propagation of cracks or pits).

To obtain EN data, three basic measurement techniques are commonly used. Potentiostatic measurement of the current noise, galvanostatic measurement of the potential noise and the measurement of potential and current noise of freely corroding electrodes (see Figure 1). In research studies investigating localized corrosion the simultaneous monitoring of current and potential noise signals is performed most frequently. Therefore a three electrode arrangement is used. Two nominally identical electrodes (working electrodes, WE) are connected via a zero-resistance ammeter (ZRA) monitoring the coupling current between the electrodes. The fluctuations in the (corrosion) potential of the coupled electrode assembly are measured using a third electrode, either a reference electrode or pseudo reference electrode (e.g., platinum sheet/spiral or a piece of metal of similar composition as the electrode assembly) [9]. The amplitudes of electrochemical current (ECN) and potential noise (EPN) are typically in the range of 10^{-6} A and 10^{-3} V, respectively.

The above very brief review of EN measurements might show the high potential of EN to get a powerful tool for in-situ corrosion monitoring, but also revealed the very high sensitivity of the noise fluctuations and thus the difficulty in the evaluation and interpretation of certain pattern of EN and its assignment to corrosion events. The current paper only tries to point to possible difficulties in the interpretation of EPN signals which were measured during intergranular corrosion (IGC) of stainless steel specimens. The detection of IGC initiation of austenitic stainless steel (SS) coupon specimens was investigated using EN measurements. The work was performed in the framework of a diploma thesis [14] of the Friedrich-Alexander-University of Erlangen-Nürnberg (Germany) at Framatome ANP GmbH Erlangen (Germany).

2 Experimental Procedure

2.1 Materials

For the EN measurements a nuclear grade austenitic SS of type AISI 347 (UNS no. S 34700) was used. The steel was stabilized by Nb with a Nb/C ratio of 10.4 and had a grain size of 1 to 2 according to ASTM. The chemical composition and mechanical properties are shown in Tables 1 and 2. To obtain a higher susceptibility to IGC the steel was sensitized for 10 h at 700 °C. An electrochemical potentiokinetic reactivation (EPR) ratio of about 10 % was measured by the double-loop EPR method according to JIS G 0580₁₉₈₆⁽¹⁾.

2.2 Specimens

For each experiment two coupons with the dimensions of 20 x 10 x 2 mm were manufactured from the same material (SS). The specimens were embedded into epoxy resin and wet-grinded up to grit 2400 paper. For EN measurements with inert specimens two platinum coupons of the same size were used instead of SS coupons.

2.3 EN Measurement Setup

The tests were performed in a double-walled glass beaker, which was located in an earth-grounded Faraday cage (see Figures 2 and 3). Due to the high noise of electrical heating devices a thermostat outside the Faraday cage was used to heat the test solution. For the EN measurements a commercial available instrument of Gamry with analyzing software (ESA400) was used⁽²⁾. The EN measurement setup was a three electrode system (see Figure 1a). The EPN was measured between the coupled WE 1 and 2 and a pseudo reference electrode (platinum spiral), whereas the ECN was recorded via a ZRA between WE 1 and 2. A platinum (pseudo) reference electrode was chosen due to the high noise level of a “normal” reference electrode (e.g., Ag/AgCl electrode). About 10 h after starting the tests (before addition of chemicals, see below) the potential of the platinum reference electrode reached a constant value and therefore seemed to be a suitable choice for the EPN measurements. The EN was recorded with a sampling rate of 10 Hz.

2.4 Environmental Parameters

After several pre-tests a 0.5 M sulfuric acid (H₂SO₄) with 3 wt% of sodium tetrathionate (Na₂S₄O₆) at a temperature of 70 °C was chosen as the test solution. Experiments with this solution revealed IGC attack without any pitting in the investigated SS specimens after only few hours at a temperature of 70 °C.

2.5 Test Procedure

To study the behavior of the EN during initiation of IGC, tests with coupons of the material described above were performed in a beaker at a temperature of 70 °C. The tests were started in deionized water, to study the behavior of the EN without any corrosion processes or environmental influence. Therefore two coupons of the investigated steel and the platinum pseudo reference electrode were immersed in the tempered (70 °C) water. After 10 to 15 h a concentrate of the test solution was added to the deionized water (sulfuric acid and sodium tetrathionate after 10 min). The experiment was finished 24 h later. For the evaluation of the EN data the standard deviation (SD) was calculated over periods of 3 min and plotted versus time. The main task of the study was to prove a cause – effect relationship between IGC initiation, and the measurable increase in EPN. Nevertheless also the ECN was analyzed to gather additional information.

⁽¹⁾ Japanese industrial standard.

⁽²⁾ ESA400 is a trade name of Gamry Instruments, Warminster, PA, USA.

3 Results and Discussion

3.1 Results of the EN Measurements

3.1.1 EN Measurements with SS specimens.

To possibly detect IGC initiation of the SS specimens the potential and the current noise were recorded during several experiments. For the evaluation of the EN data different methods were analyzed. The most promising method was the calculation of the SD. The SD of the EPN and ECN was calculated for 3 min intervals and plotted versus the time. This provided a quantitative measure of the fluctuation amplitudes, i.e., the noise level. Figure 4 shows the typical course of the SD of the EPN and ECN during the performed tests. 1 to 2 h after addition of the test solution the SD of the EPN reached the same values than in deionized water, whereas the SD increased after 6 to 10 h to values of about 0.7 mV. A lower amplitude of the EPN was then observed about 15 h after chemical addition. Figure 5 shows two examples of the EPN raw signals 3 and 8 h after addition of test solution. Initially it was concluded, that the peak of the SD was related to IG attack, as metallographic examination of the specimens by light microscope after the tests revealed IGC (see Figure 6a). But metallographic investigations of the specimens taken out of the test solution 3 h after addition of the chemicals showed already first signs of IGC (see Figure 6b). Therefore the increase in EPN must have been influenced by other phenomena than IGC.

Although the main task was to investigate the behavior of the EPN during initiation of IGC, also the ECN signal was analyzed similar to the EPN. 3 to 4 h after addition of the test solution an increase of the ECN SD was observed. These higher ECN fluctuation amplitudes fitted very well to the corrosion behavior of the investigated specimens. Therefore the ECN could be related to initiation processes of IGC. After about 10 h the SD of the ECN dropped off significantly to values of about 7 nA. This was explained by the reduced IGC attack at this stage until the end of the experiment, which was observed by metallographic investigations of specimens taken out of the test solution at different times.

To double-check whether the increase in EPN during the tests was caused or at least influenced by IGC processes or not, tests with inert specimens (platinum coupons) were performed under otherwise identical conditions and experimental procedure.

3.1.2 EN Measurements with Inert (Pt) Specimen.

The EN data were evaluated the same way as during the tests with the SS specimens. Figure 7 shows the typical course of the SD of the EPN and ECN. Basically the SD of the EPN showed the same behavior as described above. The EPN increased 7 to 11 h after addition of the test solution, although to a lower extent ($SD_{max} \approx 0.4$ mV), before it decreased after further 2 to 4 h. As the platinum coupons revealed no corrosion attack the bigger amplitude of the EPN could not exclusively be caused by IGC.

The SD of the ECN showed no or only minor peaks, although the noise amplitude also increased slightly after 7 to 10 h of chemical addition to a steady state value of about 5 nA. It is believed that this could be the result of continuing electrochemical reactions of the thionate.

3.2 Effect of Sulfur Chemistry on the EN Measurements

Sulfur containing compounds like thiosulfates, tetrathionates or the Wackenroder Liquid (saturated and aged solution of hydrogen sulfide and sulfur dioxide) are known to induce IG attack or stress corrosion cracking (SCC) on austenitic SS in aqueous solutions at ambient or slightly elevated temperatures. Therefore these kinds of reagents seem to be a very convenient way to perform IGC or SCC experiments in the laboratory and for creating reproducible environmental conditions where SCC (or IGC) occurs and can be monitored in appropriate time periods. For studying SCC reactions and mechanisms the EN measurement technique seems to be the best choice, because the electrode potentials are not distorted by an outer signal and therefore the electrochemical reactions between metal surface and solution remain at the same state.

When studying IGC or SCC by using thionates their chemistry should not be disregarded. Most often thiosulfates or tetrathionates, like in this study, are used for the experiments. Thiosulfates and tetrathionates are coupled by the following redox reaction [15, 16]:

This reaction is well known and commonly used in analytical chemistry (iodometry) [15].

Thiosulfates, especially in acidic solutions, are not stable and decompose. In the presence of water hydrogen sulfide is oxidized by sulfur trioxide, finally forming sulfur and sulfur dioxide:

Also thiosulfates formed with heavy metals decompose spontaneously, e.g. [15]:

Stronger oxidants like chlorine or oxygen can oxidize thiosulfates directly to sulfates:

All the reactions mentioned above may continue in the bulk solution. No presence of metal interfaces is needed. Based on equations 2 and 3 it can be seen that three different compounds are formed if thiosulfates decompose: hydrogen sulfide (gas), sulfur dioxide (gas), and sulfur (colloidal). Therefore the metallic interfaces of the electrodes and the beaker surface as well can act as condensation nuclei for the different reaction products when thiosulfate decomposes, due to their surface roughness and edges, etc. The gas bubbles formed on the electrodes are not necessarily visible, and most probably diffuse into the solution where they are dissolved. The colloidal sulfur trickles down to the beakers bottom. All these processes cause changes in the conductivity, the density of the solution and of course in the electrical field between reference and working electrode and therefore produce noise over the whole frequency range as long the reactions in the solution continue [17]. Furthermore the production of hydrogen sulfide and sulfur dioxide gas can result in changes of the potential of the platinum reference electrode and influence the EN signal additionally.

For that reason it is questionable if the EPN of the corrosion reaction, especially if measured with platinum reference electrodes, in solutions containing thionate can be identified in the “other” noise or if anything at all is monitored that can be ascribed to the IGC of SS. Due to limitation in time it was not possible to perform solution chemistry measurements in the framework of the current EN study to further verify the influence of electrochemistry of thionates on the EN.

“...sulfur is a devilish substance...Discharged from the bowels of the earth, by volcanoes or evil-smelling hot springs...Surely the effluent of Hell itself.” – J.R. Postgate

4 Summary and Conclusions

The detection of intergranular corrosion (IGC) initiation of austenitic stainless steel (AISI 347) coupon specimens was investigated using electrochemical noise (EN) measurements with focus on the electrochemical potential noise (EPN). The corrosion tests were performed in acidic sodium tetrathionate ($\text{Na}_2\text{S}_4\text{O}_6$) solution. A peak in the EPN signal was observed after several hours of immersion of the specimens to the test solution. To confirm whether the observed increase in the EPN fluctuations during the tests were caused by IGC processes or not, similar tests with platinum specimens were performed. Due to these tests and investigations of the specimens by light microscope it was concluded that the IGC initiation in tetrathionate solution could not be detected by EPN due to interference of the noise signal with chemical processes which occurred in the test solution. Furthermore the platinum reference electrode might have had an additional influence on the EPN. Notwithstanding, the current noise seemed to be more suitable to detect IGC of the investigated stainless steel specimens. Therefore EN measurements are still a very powerful corrosion monitoring tool, although EN results obtained by tests in thionate or similar sulfur containing solutions should always be regarded with great care and verified, e.g., by tests with inert specimens.

5 Acknowledgment

The support for this work by Prof. Dr. E. Wendler-Kalsch (Friedrich-Alexander-University Erlangen-Nürnberg, Germany) and W. Straub (Siemens, Erlangen, Germany) is gratefully acknowledged.

6 References

- [1] W.P. Iverson, *Nature* **1967**, 213, p. 486.
- [2] W.P. Iverson, *Journal of the Electrochemical Society* **1968**, 115, p. 617.
- [3] V.A Tyagai, N.B. Lukyanchikova, *Elektrokhimija* **1967**, 3, p. 316.
- [4] V.A Tyagai, *Elektrokhimija* **1967**, 3, p. 1331.
- [5] V.A. Tyagai, N.B. Lukyanchikova, *Surface Science* **1968**, 12, p. 331.
- [6] V.A. Tyagai, G.Ya. Kolbasov, *Surface Science* **1971**, 28, p. 423.
- [7] J. Göllner, A. Burkert, *Materials and Corrosion* **1998**, 49, p. 614.
- [8] J.R. Kearns, J.R. Scully, P.R. Roberge, D.L. Reichert, J.L. Dawson, eds., *Electrochemical Noise Measurements for Corrosion Applications*, ASTM STP 1277, West Conshohocken, PA: American Society for Testing and Materials, **1996**.
- [9] J.L. Dawson, "Electrochemical Noise Measurement: The definitive In-Situ Technique for Corrosion Applications?", in *Electrochemical Noise Measurement for Corrosion Applications*, ASTM STP 1277, eds. J.R. Kearns, J.R. Scully, P.R. Roberge, D.L. Reichert, J.L. Dawson, West Conshohocken, PA: American Society for Testing and Materials, **1996**, p. 3.
- [10] J. Hickling, D.F. Taylor, P.L. Andresen, *Materials and Corrosion* **1998**, 49, p. 651.
- [11] D.A. Eden, "Electrochemical Noise – the First Two Octaves", *CORROSION/98*, Paper No. 386, Houston, TX, USA, NACE International, **1998**.
- [12] G.L. Edgemon, G.E.C. Bell, "Problems, Pitfalls and Probes: Welcome to the Jungle of Electrochemical Noise Technology", *CORROSION/98*, Paper No. 383, Houston, TX, USA, NACE International, **1998**.
- [13] G. Schmitt, P. Plagemann, *Materials and Corrosion* **1998**, 49, p. 677.
- [14] S. Ritter, "Detektion lokaler Korrosionserscheinungen mit elektrochemischen Rauschmessungen", *Diploma Thesis*, Friedrich-Alexander-University of Erlangen-Nürnberg, Germany, April **2000**.
- [15] M. Schmidt, *Anorganische Chemie*, Band 1, Bibliographisches Institut Mannheim, **1984**.
- [16] *Gmelins Handbuch der Anorganischen Chemie*, Band Schwefel, Verlag Chemie, **1986**.
- [17] F. Huet, M. Jerome, P. Manolatos, F. Wenger, "Influence of Hydrogen Absorption on the Electrochemical Potential Noise of an Iron Electrode under Corrosion with Gas Evolution", in *Electrochemical Noise Measurement for Corrosion Applications*, ASTM STP 1277, eds. J.R. Kearns, J.R. Scully, P.R. Roberge, D.L. Reichert, J.L. Dawson, West Conshohocken, PA: American Society for Testing and Materials, **1996**, p. 375.

Tab. 1. Chemical composition of the investigated stainless steel in wt%.

Tab. 1. Chemische Zusammensetzung des untersuchten rostfreien Stahls in Gew.%.

AISI 347 (UNS No.: S 34700, German Standard No.: 1.4550)	C	Si	Mn	Cr	Mo
Heat treatment: 1300 °C/30 min/water quenched + 700 °C/10 h/water quenched	0.075	0.520	1.170	17.850	0.610
	P	S	Ni	Nb	Ti
	0.027	0.024	10.500	0.780	<0.030

Tab. 2. Mechanical properties (tensile tests in air, DIN 50125 standard, $R_{p0.2}$ = yield stress, R_m = tensile strength, A_5 = elongation at fracture, Z = reduction of area).

Tab. 2. Mechanische Eigenschaften (Zugversuche an Luft nach DIN 50125, $R_{p0.2}$ = Streckgrenze, R_m = Zugfestigkeit, A_5 = Bruchdehnung, Z = Brucheinschnürung).

	Room temperature				280 °C			
	$R_{p0.2}$ [MPa]	R_m [MPa]	A_5 [%]	Z [%]	$R_{p0.2}$ [MPa]	R_m [MPa]	A_5 [%]	Z [%]
AISI 347 (UNS No.: S 34700)	265	583	46.5	38	201	462	34.5	44

Fig. 1. Schematic drawing of the three basic electrochemical noise measurement techniques: a) Measurement of potential and current noise of freely corroding electrodes, b) galvanostatic measurement of the potential noise, c) potentiostatic measurement of the current noise. WE = working electrode, RE = reference electrode, CE = counter electrode.

Abb. 1. Schematische Zeichnung der drei grundlegenden elektrochemischen Rauschmesstechniken: a) Messung des Potential- und Stromrauschens unter aussenstromlosen Bedingungen, b) galvanostatische Messung des Potentialrauschens, c) potentiostatische Messung des Stromrauschens. WE = Arbeitselektrode, RE = Referenzelektrode, CE = Gegenelektrode.

Fig. 2. Schematic drawing of the three electrode electrochemical noise measurement setup which was used for the experiments.

Abb. 2. Schematische Zeichnung der Drei-Elektroden-Anordnung, die für die elektrochemischen Rauschmessungen eingesetzt wurde.

Fig. 3. Photograph of the EN measurement setup with electrochemical noise measurement device (left), double-walled glass beaker, thermostat and Faraday cage.

Abb. 3. Bild des Versuchsaufbaus mit Rauschmessgerät (links), doppelwandigem Becherglas, Thermostat und Faradaykäfig.

Fig. 4. Standard deviation of the potential (left) and current (right) noise calculated over periods of 3 min. WE 1 and 2: AISI 347 coupons, test solution: deionized water/0.5 M H_2SO_4 + 3 wt% $\text{Na}_2\text{S}_4\text{O}_6$, $T = 70^\circ\text{C}$, sampling rate: 10 Hz.

Abb. 4. Standardabweichung des Potential- (links) und Stromrauschens (rechts), berechnet über Intervalle von 3 Min. WE 1 und 2: 1.4550-Coupons, Versuchslösung: demineralisiertes Wasser/0.5 M H_2SO_4 + 3 Gew.% $\text{Na}_2\text{S}_4\text{O}_6$, $T = 70^\circ\text{C}$, Abtastrate: 10 Hz.

Fig. 5. Two examples of the electrochemical potential noise (EPN) 3 h (left) and 8 h (right) after addition of chemicals. WE 1 and 2: AISI 347 coupons, test solution: 0.5 M H_2SO_4 + 3 wt% $\text{Na}_2\text{S}_4\text{O}_6$, $T = 70^\circ\text{C}$, sampling rate: 10 Hz.

Abb. 5. Zwei Beispiele des Potentialrauschens (EPN) 3 h (links) und 8 h (rechts) nach Zugabe der Chemikalien. WE 1 und 2: 1.4550-Coupons, Versuchslösung: 0.5 M H_2SO_4 + 3 Gew.% $\text{Na}_2\text{S}_4\text{O}_6$, $T = 70^\circ\text{C}$, Abtastrate: 10 Hz.

Fig. 6. Micrographs of metallographic cross sections, grain boundaries etched, AISI 347. a) After 24 h at 70°C in test solution (0.5 M H₂SO₄ + 3 wt% Na₂S₄O₆), b) after 3 h at 70°C in test solution. Magnification: 150:1.

Abb. 6. Lichtmikroskopische Aufnahmen von metallographischen Querschliffen, Korngrenzen angeätzt, 1.4550. a) Nach 24 h in Versuchslösung bei 70 °C (0.5 M H₂SO₄ + 3 Gew.% Na₂S₄O₆), b) nach 3 h in Versuchslösung bei 70 °C. Vergrößerung: 150:1.

Fig. 7. Standard deviation of the potential (left) and current (right) noise calculated over periods of 3 min. WE 1 and 2: platinum coupons, test solution: deionized water/0.5 M H₂SO₄ + 3 wt% Na₂S₄O₆, T = 70 °C, sampling rate: 10 Hz.

Abb. 7. Standardabweichung des Potential- (links) und Stromrauschens (rechts), berechnet über Intervalle von 3 Min. WE 1 und 2: Platin-Coupons, Versuchslösung: demineralisiertes Wasser/0.5 M H₂SO₄ + 3 Gew.% Na₂S₄O₆, T = 70 °C, Abtastrate: 10 Hz.