# Evaluation of Electrochemical Noise Parameters as Indicators of Stress Corrosion Crack Initiation and Propagation of Alloy 600 SG Tube at High Temperature

Sung Woo Kim*, Hong Pyo Kim, Pyung Sik Choi
*Nuclear Materials Research Division, Korea Atomic Energy Research Institute, 1045 Daedeokdaero, Yuseong-gu, Daejeon, 305-353, Korea*
**Corresponding author: kimsw@kaeri.re.kr*

## 1. Introduction

It has been reported that an electrochemical noise (EN) technique is powerful enough to distinguish between different types of localized corrosions such as a pitting, crevice corrosion and stress corrosion cracking (SCC). In our previous works [1, 2], the EN data were successfully analyzed based on a stochastic theory using a probability of the EN parameters such as the frequency of events, mean free time-to-failure, Weibull shape parameter. In this respect, the present work is aimed at developing evaluation method of the EN parameters as indicators of SCC initiation and propagation of Alloy 600 steam generator (SG) tubing in a pressurized water reactor (PWR).

## 2. Experimental

EN measurement was carried out with a Zahner IM6e equipped with a Zahner NProbe. Two Alloy 600 C-ring specimens were galvanically coupled using the zero-resistance ammeter (ZRA) mode of IM6e. These C-ring were manufactured from an Alloy 600 SG tubing as low temperature mill-annealed (LTMA) with an outer diameter of 22.23 mm and a thickness of 1.27 mm according to ASTM G38. One was stressed to 150% of its room temperature YS at the apex using an Alloy 600 bolt and nut, and the other was unstressed.

EN measurements were performed in two different modes: one is a potential-controlled current noise (PCCN) mode and the other is an open circuit potential noise (OCPN) mode. In PCCN mode, only electrochemical current noise (ECN) is measurable. ECN was recorded by applying anodic potential of 100 mV vs. a reference electrode (a pure Ni wire with 1 mm diameter) in a 40 wt% NaOH solution containing only 10,000 ppm PbO for 100 h at 315 $^{o}$C. In OCPN mode, both electrochemical potential noise (EPN) and ECN of the specimens can be recorded simultaneously. EPN and ECN were recorded with an external Ag/AgCl reference electrode filled with a 0.1 M KCl solution, first in a 40 wt% NaOH solution containing 10,000 ppm PbO for 264 h at 290 $^{o}$C. After that, 500 ppm CuO was added to the solution and then EPN and ECN were recorded for 136 h at 290 $^{o}$C further.

After an entire immersion test, the specimens were chemically etched with a solution of 2% bromine + 98% methanol, and then they were examined by a scanning electron microscopy (SEM, JEOL JSM-6360) equipped with an energy dispersive spectrometer (EDS, Oxford-7582).

## 3. Results and Discussion

### *3.1 Analysis of ECN in PCCN mode*

Fig. 1 presents the time record of ECN measured in PCCN mode by applying an anodic potential of 100 mV(vs. Ni/NiO) in a 40 wt% NaOH solution containing only 10,000 ppm PbO at 315 $^{o}$C. After 36 h immersion in the solution, a change in fluctuation of current was detected. From the SEM analysis of the apex of the C-ring specimen, it was found that a surface oxide film was locally broken down and also some small cracks were initiated in micron-scale along grain boundary. As shown in Fig. 1, the amplitude, mean value and time interval of ECN recorded from 36 to 44 h were remarkably increased as compared to ECN just before. It is obvious that those changes in ECN are attributable to the initiation of SCC in the caustic solution.

After the entire immersion test for 100 h, it was confirmed that one of those small cracks was propagated in an intergranular (IG) mode from the SEM analysis. In Fig. 1, similar increases of the amplitude and mean value of ECN were detected from 50 to 66 h except decrease of the time interval of ECN as compared to those of ECN recorded from 36 to 44 h. It is strongly suggested that those changes in ECN are mainly due to the propagation of SCC in the caustic solution.

Fig. 2 gives the plot of power spectral density (PSD) vs. frequency converted from the time record of ECN by a fast Fourier transformation (FFT). It was clearly seen that the value of PSD, i.e., the amplitude of ECN generated during the initiation of SCC (B and C in Fig. 2) was higher than that measured before the initiation of SCC where the uniform corrosion is expected to be dominant (A in Fig. 2) at whole frequency ranges. Moreover, the value of PSD during the propagation of SCC (D, E and F in Fig. 2) was higher than that obtained after the propagation of SCC (G in Fig. 2) at low- and medium-frequency ranges.

### *3.2 Analysis of EPN and ECN in OCPN mode*

After the immersion test in the caustic solution containing both PbO and CuO for 430 hrs in total at 290 $^{o}$C, it was found that several cracks were propagated in IG mode from SEM analysis of the C-ring specimen. In the time records of EPN and ECN measured in OCPN mode, there were typical potential drops in EPN with simultaneous current rises in ECN, which have generally been observed during localized corrosions such as the pitting, crevice corrosion, intergranular corrosion and SCC.

From the analysis of EPN and ECN obtained from the C-ring specimen in the caustic solution containing both PbO and CuO in OCPN mode, it is strongly suggested that the random potential drop with a shorter time interval accompanied by a repetitive current increase with a lower amplitude in a stepwise manner is attributable to the initiation of SCC composed of a local break-down and repassivation of a surface oxide film, whereas the potential drop with a longer time interval accompanied by a current increase with a larger amplitude is mainly due to the propagation of SCC.

Based on a shot-noise theory [3], the frequency of events $f_n$ of the localized corrosions is estimated for each time record as given by,

$$f_n = B^2/(\Psi_E A) \quad (1),$$

where $B$ is the Stern-Geary coefficient, $\Psi_E$ the PSD value of the EPN obtained by averaging several of the low-frequency points using the FFT algorithm and $A$ represents the exposed electrode area. From a set of $f_n$ calculated from the PSD plots according to Eq. (1), the cumulative probability $F(f_n)$ at each $f_n$ is determined numerically by a mean rank approximation [3]. In this work, to understand the stochastic characteristics of SCC, the probability of $f_n$ was analyzed using the Weibull distribution function [1, 2] which is one of the most commonly used cumulative probability functions for predicting a life and failure rate expressed as,

$$\ln\{\ln[1/(1-F(t_n))]\} = m \ln t_n - \ln n \quad (2),$$

where $t$ is the mean free time-to-failure corresponding to $1/f_n$, and $m$ and $n$ represent the shape and scale parameters, respectively.

From the comparison between the microscopic and electrochemical noise analysis, EN parameters such as $f_n$, $t_n$ and $m$ will be discussed in detail in terms of the initiation and propagation of SCC.

## 4. Conclusion

From the analysis of EPN and ECN obtained from the Alloy 600 SG tube materials in the simulated caustic solution environment of SG sludge piles at a high temperature, it is strongly suggested that EN parameters can be indicatives of the initiation and propagation of SCC differentially.

## REFERENCES

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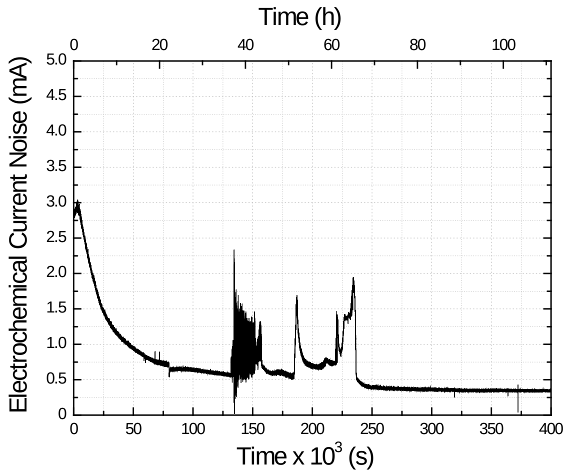


Fig. 1. Time records of ECN measured in PCCN mode from the stressed C-ring specimens in the solution containing PbO.

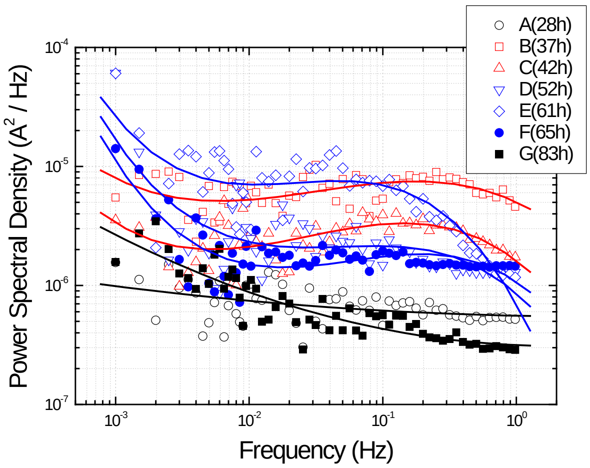


Fig. 2. Plots of power spectral density vs. frequency converted from time records of ECN measured in PCCN mode.