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IN-SITU MONITORING OF MICRO-CRACKING OF Ni-BASED ALLOYS AT HIGH TEMPERATURE USING ELECTROCHEMICAL NOISE TECHNIQUE

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Abstract. This work is aimed to establish *in-situ* technique to monitor stress corrosion cracking of nickel-based alloys in a micro-scale at high temperature using an electrochemical noise analysis based on a stochastic theory. The electrochemical current noise was measured from Alloy 600 steam generator tubing. The amplitude and frequency in time domain, the power spectral density in frequency domain, and the mean time-to-failure were analyzed in terms of the micro-cracking and the crack growth of nickel-based alloys at high temperature.

1. INTRODUCTION

Although nickel-based alloys and stainless steels have been used as various components in a pressurized water reactor (PWR) due to their high corrosion resistance, many forms of stress corrosion cracking (SCC) have been reported in specific conditions of materials and pressurized water environments. Many researchers have devoted their time to predict the service life of those components based on the crack growth rate. However, there have been little efforts to distinguish the initiation of SCC in a nano- or micro-scale due to the difficulty in its detection or monitoring, even though overall time-to-failure is mainly controlled by the crack initiation time not by the crack growth time. Recently, there was an approach to investigate the SCC mechanism by distinguishing between the initiation and propagation stages using an electrochemical noise (EN) technique in a nano- or micro-scale [1,2]. The EN is defined as a fluctuation of the electrochemical potential (EPN) or current (ECN) which is observed experimentally to be associated with localized corrosion processes [3,4].

Therefore the present work is aimed to establish *in-situ* technique to monitor SCC of nickel-based alloys in a micro-scale at high temperature using the EN analysis based on a stochastic theory. In the highly caustic solution containing lead oxide, the ECN was measured from C-ring specimens of Alloy 600 materials by applying an anodic potential. From the ECN measured in time record, the power spectral density was calculated in frequency domain by a fast Fourier transformation. Finally the mean time-to-failure was analyzed based on the stochastic theory to differentiate the micro-cracking from the crack growth as well as the general corrosion.

2. EXPERIMENTAL

Alloy 600 steam generator (SG) tubing (Valinox Heat No. NX8527) with 22.23 mm outer diameter (OD), 1.27 mm thickness was used for this work. Alloy 600 tubing was pilgered by the manufacturer, and heat treated at 920 °C for 15 min in an Ar-filled quartz capsule in a furnace, followed by water quenching, to simulate low-temperature mill-annealing (LTMA).

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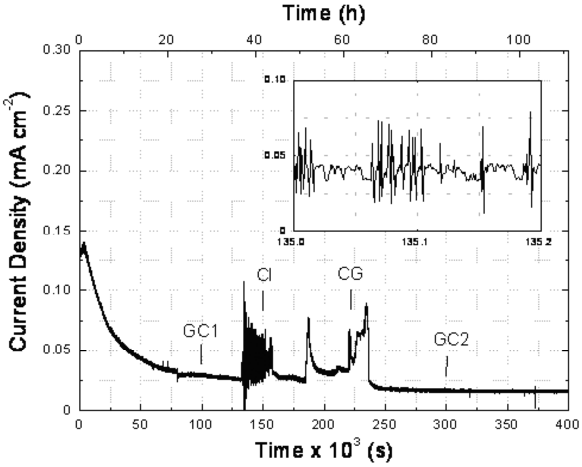

Fig. 1. Time record of the ECN measured in the PCCN mode from the stressed C-ring specimen in a 40 wt.% NaOH solution containing 0.01 wt.% PbO at 315 °C for 110 h.

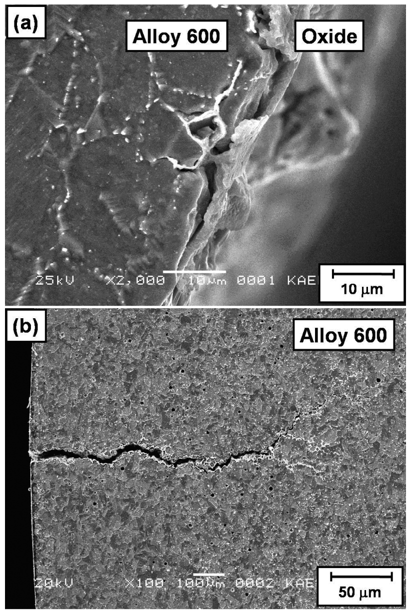

Fig. 2. SEM micrographs of the side surface of the C-ring apex after the immersion times of (a) 42 h and (b) 110 h in the leaded caustic solution at 315 °C.

The C-ring specimens were fabricated from the SG tubings in accordance with the ASTM G38 standard. The OD surface of the specimens was ground by #2000 emery paper, and then cleaned with ethanol and water in sequence. The C-ring specimen was stressed to 150% of its room temperature yield strength (YS) at the apex using bolt and nut of the same material. The test environment was an aqueous solution of 40 wt.% NaOH containing 0.01 wt% PbO (leaded caustic solution) at 315 °C. Prior to the immersion test, the test solution was deaerated with 99.99% nitrogen gas for 20 h.

The EN measurement was carried out with Zahner IM6e equipped with Zahner Nprobe as described in detail in our previous report [1]. In the potentiostatic-controlled current noise (PCCN) mode, only ECN was recorded between the stressed and unstressed specimens during applying an anodic potential of 100 mV vs. open circuit potential (OCP) to maintain the electrode potential near the active-passive transition range for Alloy 600 in the caustic environment. The reference electrode was 1 mm in diameter of the same material to be tested. The sampling interval and frequency bandwidth were 0.5 s and 1 mHz ~ 1 Hz, respectively. The power spectral density and frequency of events were calculated from each set of time records that consisted of 2,048 data points acquired for 1×10^3 s.

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

3. RESULTS AND DISCUSSION

Fig. 1 gives the time record of the ECN obtained from the stressed C-ring specimen in the leaded caustic solution at 315 °C for 110 h in the PCCN mode of the EN measurement. The ECN changed abruptly after immersion for 132×10^3 s, which has generally been observed during localized corrosions such as pitting corrosion, crevice corrosion and SCC [1-4]. As shown in detail in the insert of Fig. 1, the ECN revealed repetitive current rises followed by fast decay with certain time interval in the time record from 132×10^3 to 158×10^3 s (CI). This means that discrete events of a localized corrosion are occurring at CI during the immersion of the C-ring in the leaded caustic solution. On the other hand, from 185×10^3 to 240×10^3 s (CG), the ECN revealed current increases followed by slower decay with longer time interval in the time record, indicating the occurrence of another localized corrosion event inducing larger charge passage than that at CI.

In order to correlate the changes of the ECN with the cracking stages, the test was interrupted and the surface of the specimen was examined for cracking at accumulated immersion times of 22, 42, and 110 h. After the immersion test in the leaded caustic solution for 22 h, any micro-cracking was not

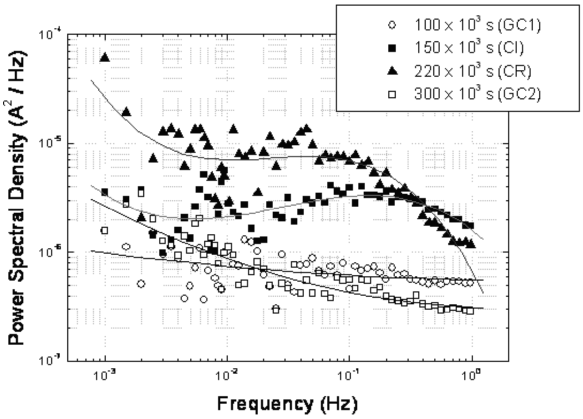

Fig. 3. Plots of the PSD vs. the frequency calculated from each time record of the ECN by the FFT algorithm at GC1, CI, CG, and GC2.

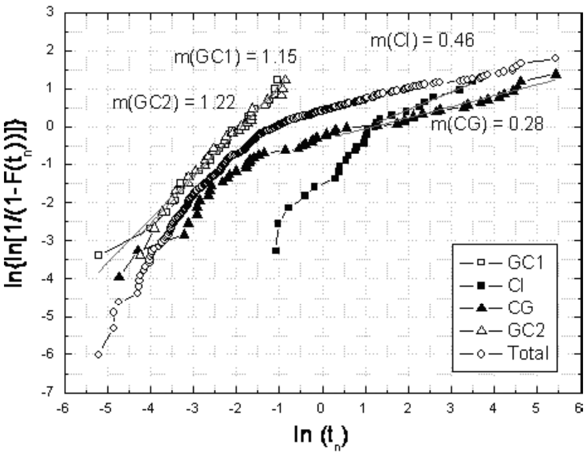

Fig. 4. Plots of ln{ln[1/(1-F(t_n))]} vs. ln t_n calculated from the sets of f_n using Ψ_I according to Eqs. (2) and (3) at various time periods.

found on the specimen surface from the extensive examination by SEM. At the accumulated immersion time of 42 h, it turned out that there were many defect sites such as local break-down of the surface oxide film and micro-cracks initiated with depth of one grain or less in the OD surface from the SEM analysis of the C-ring apex as shown in Fig. 2a. After the entire immersion test for 110 h, one of micro-cracks was propagated as presented in Fig. 2b. The crack grew in an intergranular (IG) mode and the crack mouth and tip were covered by a surface oxide film, which is typical of SCC of Alloy 600 in leaded caustic environments [5-7]. With the aid of the SEM analysis, it is easily anticipated that the current rises followed by steeper decay with shorter time interval in the time record of the ECN at CI in Fig. 1 are attributable to the micro-cracking, that is, the initiation of SCC, whereas the current increases followed by slower decay with longer time interval in the time record at CG in Fig. 1 are mainly due to the crack growth. The steady-state current response of the ECN at GC1 and GC2 in Fig. 1 indicates that only general corrosion (the passive oxide film formation) is expected to occur.

Fig. 3 presents the plots of the power spectral density (PSD) vs. the frequency calculated from each time record of the ECN by a fast Fourier transform (FFT) algorithm at CG1, CI, CG, and CG2, respectively. The PSD value of the ECN obtained at CI where the micro-cracking is supposed to occur, was higher at whole frequency range than that obtained at CG1 and CG2 where only general corrosion occurs on the C-ring surface. Similar behavior was found in the PSD of the ECN obtained at CG where the crack is anticipated to propagate, except the remarkable increase of the PSD at a low frequency limit. The increases of the PSD, especially at lower frequency range, strongly indicates the increase in the number of localized corrosion events, that is, the micro-cracking and the crack growth, respectively, as previously reported [1,2].

To evaluate the stochastic characteristics of the micro-cracking and the crack growth of Alloy 600 SG tubing in high temperature caustic solution in this work, a shot-noise analysis was employed under the assumption that the ECN is independently generated by the individual event of localized corrosion. Based on the shot-noise theory [3,4], the frequency of events f_n of the localized corrosion is generally determined from the time record of the EPN as given by

$$f_n = B^2 / \left(\Psi_E \times A\right), \tag{1}$$

where B is the Stern-Geary coefficient, Ψ_E the PSD value of the EPN at lower frequency limit and A represents the exposed electrode area. From a set of f_n calculated from the PSD plots of the EPN according to Eq. (1), the cumulative probability $F(f_n)$ at each f_n is determined numerically by a mean rank approximation [3]. However, this statistical approach using the EPN can not be readily applied in this work because only ECN is recorded in the PCCN mode of the EN measurement. In the present work, therefore, new approach using the PSD value of the ECN at lower frequency limit Ψ_I is established from a relationship between Ψ_I and Ψ_E ($\Psi_E = \Psi_I \times R_n^2$) as given by,

$$f_n = B^2 / \left(\Psi_I \times R_n^2 \times A\right), \tag{2}$$

where Ψ_I is the PSD value of the ECN at lower frequency limit, calculated by averaging several low-frequency points using the FFT algorithm, and R_n represents the noise resistance. In this work, the value of R_n was calculated from Ψ_I and Ψ_E which were reported in our previous works on the analysis of EPN and ECN measured from Alloy 600 SG tubing at OCP in the same test condition [1,2].

The probability of f_n for micro-cracking was analyzed using the Weibull distribution function, the most commonly used cumulative probability function for predicting a life and failure rate [1,2,8,9]. Using the Weibull distribution function, the probability of the mean time-to-failure t_n which corresponds to $1/f_n$ is expressed as,

$$\ln\{\ln[1/(1-F(t_n))]\} = m\ln t_n - \ln n, \qquad (3)$$

where m and n are the shape and scale parameters, respectively.

Fig. 4 presents the plots of $\ln\{\ln[1/(1-F(t_n))]\}$ vs. $\ln t_n$ calculated from the sets of t_n at GC1, CI, CG and GC2 according to Eqs. (2) and (3). The Weibull probability plot at points CI and CG showed two linear regions, while that plot at points GC1 and GC2 revealed a straight line. The two linear regions are likely to indicate that two failure modes with different characteristic time-to-failure exist at the time period. Consequently, it was easily anticipated that the slope in the longer range of t_n is responsible for the localized corrosions such as the micro-cracking (CI) and the crack growth (CG) when compared to the slope in the shorter range of t_n which is similar to that slope for the general corrosion (GC1 and GC2).

In our previous works [1,2,8,9], it was also reported that the shape parameter m of the Weibull plot of t_n calculated from Ψ_E according to Eqs. (1) and (3) can be regarded as an indicator of types of corrosion in the high temperature caustic solution; the values of m determined from the Weibull plot by a linear curve fitting method were 1.46~1.70 for the general corrosion, 0.59~0.78 for the micro-cracking, and 0.16~0.18 for the crack growth. It should be noted that the values of m calculated from Ψ_I according to Eqs. (2) and (3) in the present work revealed good agreement with those values previous reported; 1.15 and 1.22 for the general corrosion at GC1 and GC2, respectively, 0.46 for the micro-cracking at CI, and 0.28 for the crack growth at CG. Therefore, it is strongly suggested that the EN analysis based on the stochastic theory is useful tool for *in-situ* monitoring of the micro-cracking of Alloy 600 SG tuing at high temperature.

4. CONCLUSIONS

From the EN and SEM analyses, it was found that the changes of the amplitude, the frequency and the PSD of the ECN were closely related to the localized corrosion events of the micro-cracking and the crack growth of Alloy 600 SG tubing in the leaded caustic solution at high temperature. From the stochastic analysis of the ECN newly approached in this work, it was suggested that the shape parameter of the Weibull plot of the time-to-failure for the micro-cracking was clearly distinguishable from that parameter for the crack growth as well as for the general corrosion.

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