ELSEVIER

Journal of Nuclear Materials 245 (1997) 201-209

journal of nuclear materials

Detection of stress corrosion cracking and general corrosion of mild steel in simulated defense nuclear waste solutions using electrochemical noise analysis

G.L. Edgemon [a], *, M.J. Danielson [b], G.E.C. Bell [c]

[a] *Lockheed Martin Hanford Corporation, P.O. Box 1970, MSIN: R1-30, Richland, WA 99352, USA*
[b] *Pacific Northwest National Laboratory, P.O. Box 999, MSIN: P8-15, Richland, WA 99352, USA*
[c] *M.J. Schiff and Associates, Inc., 1291 North Indian Hill Boulevard, Claremont, CA 91711, USA*

Received 19 June 1996; accepted 2 January 1997

Abstract

Underground waste tanks fabricated from mild steel store more than 253 million liters of high level radioactive waste from 50 years of weapons production at the Hanford Site. The probable modes of corrosion failures are reported as nitrate stress corrosion cracking and pitting. In an effort to develop a waste tank corrosion monitoring system, laboratory tests were conducted to characterize electrochemical noise data for both uniform and localized corrosion of mild steel and other materials in simulated waste environments. The simulated waste solutions were primarily composed of ammonium nitrate or sodium nitrate and were held at approximately 97°C. The electrochemical noise of freely corroding specimens was monitored, recorded and analyzed for periods ranging between 10 and 500 h. At the end of each test period, the specimens were examined to correlate electrochemical noise data with corrosion damage. Data characteristic of uniform corrosion and stress corrosion cracking are presented.

1. Introduction and background

The Hanford Site has 177 underground waste tanks that store approximately 253 million liters of radioactive waste from 50 years of weapons production [1]. Twenty-eight (28) tanks have a double-shell and are constructed of welded ASTM A537-Class 1 (UNS K02400), ASTM A515-Grade 60 (UNS K02401), or ASTM A516-Grade 60 (UNS K02100) material. The inner tanks of the double-shell tanks were stress relieved following fabrication. One hundred and forty-nine (149) tanks have a single shell constructed of welded mild steel, but were not stress relieved following fabrication. Tank waste is in liquid, solid, and sludge forms. Tanks also contain a vapor space above the solid and liquid waste regions. The composition of the waste varies from tank to tank but generally has a high pH (> 12) and contains sodium nitrate, sodium hydroxide, sodium nitrite, and other minor radioactive constituents resulting from plutonium separation processes [1-4]. Leaks began to appear in the single-shell tanks shortly after the introduction of untreated nitrate-based wastes in the 1950s. Leaks are now suspected to be present in a significant number of single-shell tanks [1]. The probable modes of corrosion failures are reported as nitrate stress corrosion cracking (SCC) and pitting [2]. Previous efforts to monitor internal corrosion of waste tank systems have included linear polarization resistance (LPR) and electrical resistance techniques [5,6]. These techniques are most effective for monitoring uniform corrosion, but are not well-suited for detection of localized corrosion (pitting and SCC). The use of electrochemical noise (EN) for monitoring waste tank corrosion was investigated by the Savannah River Site, but the tests were not conclusive [7].

For many years, EN has been observed during corro-

---

* Corresponding author. Tel.: + 1-509 373 7214; fax: + 1-509 373 1050.

PII S0022-3115(97)00005-6

sion and other electrochemical reactions, and the phenomenon is well established [8–19]. Typically, EN consists of low frequency (< 1 Hz) and small amplitude signals that are spontaneously generated by electrochemical reactions occurring at corroding or other surfaces [20]. Laboratory studies and recent reports on field applications have reported that EN analysis is well suited for monitoring and identifying the onset of localized corrosion, and for measuring uniform corrosion rates [14–27]. A typical EN based corrosion-monitoring system measures instantaneous fluctuations in corrosion current and potential between nominally identical electrodes of the material of interest in the test environment of interest. Time-dependent fluctuations in corrosion current are described by electrochemical current noise, and time-dependent fluctuations of corrosion potential are described by electrochemical potential noise. It has been shown that each type of corrosion phenomenon presents a unique relationship between corrosion current and potential transients in the temporal data [8–27]. Other methods of analysis involve transforming temporal data to the frequency domain for analysis [28].

High rates of localized or uniform corrosion probably occur infrequently, if ever, in waste tanks under 'normal' or reference waste tank chemistry conditions. This conclusion is supported by previous testing and more than 400 tank-years of operation at the Hanford Site under the current double-shell tank chemistry controls [1–3]. In the reference case, sodium hydroxide is added to the nitrate-based waste. The carbon steel forming the tank walls is passive under these conditions, resulting in little corrosion activity. However, waste tank chemistry is subject to change over time due to radiolysis and other ongoing chemical reactions. In an effort to better understand the changes in corrosion behavior as a result of changes in waste chemistry, a corrosion-monitoring system using EN as a monitoring technique is being developed for deployment into a double-shell tank at the Hanford Site. The system is expected to measure uniform corrosion rates and to detect the onset of localized corrosion phenomena if tank conditions should change to allow these phenomena to occur.

Since reference waste tank chemistries will not induce localized corrosion, it was necessary to induce the desired forms of corrosion during laboratory testing by using 'off-normal' simulated waste solutions to chemically shift the potential into the range where each form of corrosion could occur. Past studies have shown nitrates to cause intergranular stress corrosion cracking (IGSCC) in carbon steel [29]. Donovan measured cracking rates of $\sim 10^{-8}$ m/s in 5.0 M $NaNO_3$ [30]. Ondrejcin showed that sodium hydroxide and sodium nitrite can inhibit the nitrate SCC process [31]. It was decided that 4 M ammonium nitrate or 5 M sodium nitrate solutions at approximately 97°C would produce SCC on the mild steels of interest with reasonably short initiation times. Simulated tank waste solutions were used to generate uniform corrosion information.

2. Test environments, equipment and procedures

The test solutions were prepared from reagent grade chemicals and demineralized water. The test environment was maintained in a three-liter, temperature-controlled test cell with appropriate openings to allow for insertion/removal of test specimens and a condenser to minimize losses caused by evaporation. The EN tests required three electrodes: a working electrode, a counter electrode, and a reference electrode. The working and counter electrodes were nominally the same material although, in these experiments, the working electrode was stressed but the counter electrode was unstressed. The working electrode was common to the measurement of corrosion current and potential. Fluctuations in corrosion current were measured between the working and counter electrodes through a zero resistance ammeter (ZRA). The sign convention of the ZRA was such that the current was positive when the working electrode was anodic (corroding) with respect to the counter electrode. The potential of the working electrode was measured with respect to a pseudo-reference of the same material. On average, the potential of the pseudo-reference is very close to that of the working electrode. Because the working electrode and the pseudo-reference electrode were connected only through a high-resistance voltmeter, a change in working electrode potential was recorded only as a potential difference between the working and pseudo-reference electrodes. Most tests did not use a standard half cell electrode.

The majority of EN data were collected with a Gamry Instruments CMS100 electrochemical measurement system and associated software [1]. Operating software scripts for this system were customized and optimized for EN data collection. Potential and current measurements were recorded once per second on the active array. Data were typically collected for 500–600 s per channel. Time delays could be inserted between data files to reduce the amount of data collected. At the conclusion of testing, internally developed statistical analysis software and Microsoft Excel [2] were used to calculate summary statistics (mean, standard deviation, and other statistical parameters) for each raw data file. The statistical parameters for each raw data file were then plotted versus elapsed time of testing to aid in data analysis. Although it is not strictly possible to distinguish between forms of corrosion using statistical data alone, statistical analysis of the raw data files can be used to identify time periods of change in corrosion behavior. By limiting preliminary data analysis to files that

---

[1] Gamry and CMS100 are trademarks of Gamry Instruments, Inc., Willow Grove, PA, USA.

[2] Microsoft and Excel are registered trademarks of Microsoft Corporation, Redmond, WA, USA.

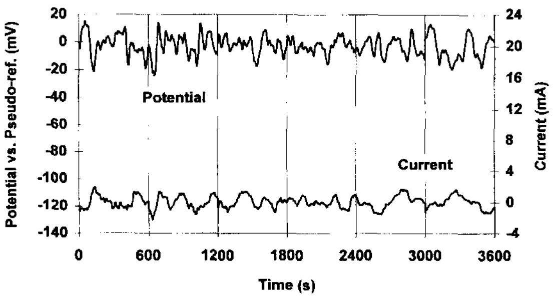

Fig. 1. Active uniform corrosion with shallow pitting prior to passivation – ASTM A516-Grade 55 pin, 4.0 M NH_4NO_3 at 97°C, 1 h of data taken after 1 h of exposure.

produced large changes in the summary statistical data, time spent on data analysis was greatly reduced.

3. Uniform corrosion test results

3.1. ASTM A516-grade 55 cylindrical pins in 4.0 M ammonium nitrate at 97°C

For this test, three identical cylindrical pins of ASTM A516-Grade 55 were used for the working, counter and pseudo-reference electrodes. The pins were approximately 6.4×10^{-3} m in diameter and 2.5×10^{-2} m in length giving a surface area of approximately 5.4×10^{-4} m^2. The test solution was brought up to 97°C and the electrodes were inserted. LPR testing shortly after specimen immersion indicated a corrosion rate of ~ 40 mpy. Fig. 1 shows 1 h of EN data collected 1 h after specimen immersion. Fig. 2 shows 1 h of data collected after 65 h of exposure. Current and potential fluctuations were random and slowly decreased in frequency and magnitude throughout the remainder of the test period. The test was terminated after approximately 96 h. The post-test surface of the working electrode is shown in Fig. 3. At the conclusion of testing, the surfaces of all three electrodes were covered with a powdery black oxide layer. Following ultrasonic cleaning in demineralized water to remove the black powdery oxide, the surfaces of the electrodes were dark brown and contained numerous shallow, 'wide' pits.

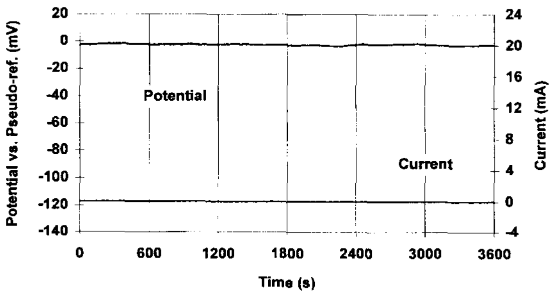

Fig. 2. Uniform corrosion after passivation, no pitting – ASTM A516-Grade 55 pin, 4.0 M NH_4NO_3 at 97°C, 1 h of data taken after 65 h of exposure.

Fig. 3. ASTM A516-Grade 55 pin showing shallow pitting – 96 h exposure, 4.0 M NH_4NO_3, 97°C.

3.2. ASTM A537-class 1 C-rings in simulated inhibited waste at 35°C

For this test, three identical C-rings of ASTM A537-Class 1 were used for the working, counter and pseudo-reference electrodes. The working electrode was strained beyond the proportional limit (near yield) shortly before testing. The C-rings were approximately 1.6×10^{-2} m in diameter, 1.6×10^{-2} m in width, and 1.6×10^{-3} m in wall thickness giving a surface area (including loading nut and bolt) of approximately 2.7×10^{-3} m^2. Test solution composition is shown in Table 1. The test solution was brought up to 35°C and the electrodes were inserted. LPR testing shortly after specimen immersion indicated a corrosion rate of less than ~ 0.1 mpy. Fig. 4 shows 1 h of EN data collected 1 h after specimen immersion. Fig. 5 shows 1 h of data collected after 65 h of exposure. Current and potential fluctuations similar to Fig. 5 were recorded throughout the remainder of the test period. The test was terminated after 497 h. The post-test surface of the work-

Table 1
Simulated inhibited waste chemistry

Constituent	Concentration (M)
$NaNO_2$	1.8
$NaNO_3$	3.6
$Na_2HPO_4 * 7H_2O$	5.0×10^{-2}
Na_2SO_4	1.4×10^{-1}
$NaAlO_2$	5.7×10^{-1}
NaF	7.6×10^{-2}
NaCl	1.1×10^{-1}
NaOH	1.9×10^{-1}

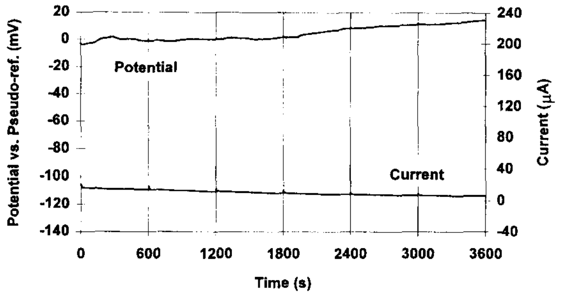

Fig. 4. Uniform corrosion after passivation – ASTM A537-Class 1 C-ring, simulated waste (see Table 1), 1 h of data taken after 1 h of exposure.

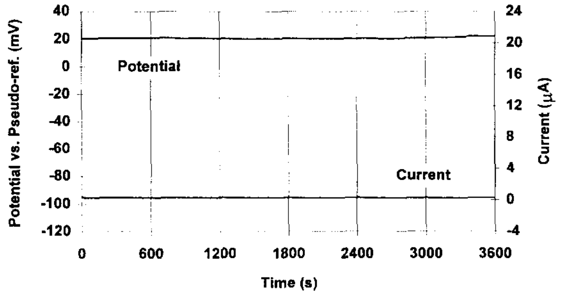

Fig. 5. Uniform corrosion after passivation – ASTM A537-Class 1 C-ring, simulated waste (see Table 1), 1 h of data taken after 65 h of exposure.

ing electrode is shown in Fig. 6. At the conclusion of testing, the surfaces of all three electrodes were shiny and bright with no evidence of pitting or other forms of localized corrosion. The original machining marks and surface scratches were still visible on the electrodes.

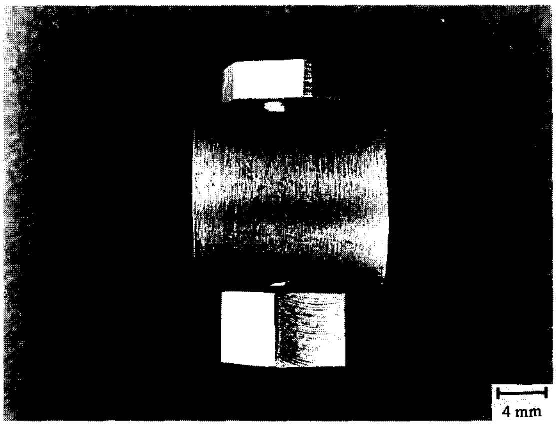

Fig. 6. ASTM A537-Class 1 C-ring – 497 h exposure, simulated waste (see Table 1), some surface scratches from machining still evident.

4. Stress corrosion cracking test results

4.1. IGSCC of ASTM A516-grade 60 U-bends in 4.0 M ammonium nitrate at 97°C

For this test, a standard ASTM A516-Grade 60 U-bend (ASTM G-58) was used as the working electrode. Flat unstressed coupons of the same material were used for the counter and pseudo-reference electrodes. All specimens were mounted in epoxy to limit the amount of exposed surface area. Approximately 1.2×10^{-3} m^2 of the counter and pseudo-reference electrode and approximately 2.4×10^{-3} m^2 of the working electrode were exposed to the ammonium nitrate solution during testing. The working electrode was strained beyond the proportional limit and mounted in epoxy approximately two days before testing. The test solution was brought up to 97°C and the electrodes were inserted. As with the A516-Grade 55 pins tested previously, current and potential fluctuations from the U-bend were random in nature, slowly decreasing in frequency and magnitude over the first 21 h of exposure. The working electrode was removed and examined under low magnification for evidence of IGSCC after approximately 21 h of exposure. No cracks were evident in the working electrode. Current and potential fluctuations over the first 21 h of testing were characteristic of uniform corrosion in a passivating system with a small amount shallow pitting occurring just after immersion.

Following inspection, the working electrode was reimmersed into the ammonium nitrate solution. At approximately 22 h into the exposure, sharp 20–60 mV drops in working electrode potential accompanied by 10–15 mA bursts of current began to occur. An hour of data collected after 29 h of exposure is shown in Fig. 7. An hour of data collected after 32 h of exposure is shown in Fig. 8. Data similar to Figs. 7 and 8 were recorded for 25 h following reimmersion. Approximately 15 transients similar to those shown in Figs. 7 and 8 were collected prior to test termination. The test was terminated after approximately 46 h. Upon removal of the working electrode, it was observed that a primary intergranular crack had propagated across the width of the electrode (~ 19 mm) and from

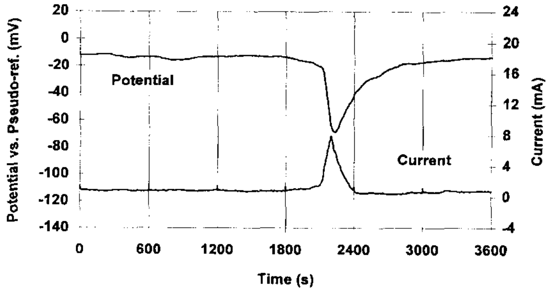

Fig. 7. SCC Propagation – ASTM A516-Grade 60 U-bend, 4.0 M NH_4NO_3 at 97°C, 1 h of data taken after 29 h of exposure.

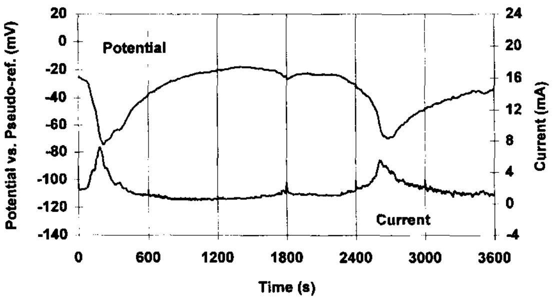

Fig. 8. SCC Propagation – ASTM A516-Grade 60 U-bend, 4.0 M NH_4NO_3 at 97°C, 1 h of data taken after 32 h of exposure.

approximately 1–2 mm in depth. The remaining surfaces of all three electrodes were smooth and covered with a dark powdery oxide. The surface of the working electrode following testing is shown in Fig. 9.

4.2. IGSCC of ASTM A537-class 1 C-rings in 4.0 M ammonium nitrate at 97°C

For this test, three identical C-rings of ASTM A537-Class 1 were used for the working, counter and pseudo-reference electrodes. The working electrode was notched, pre-cracked by cyclic fatigue, and strained beyond the proportional limit shortly before testing. The working electrode was strained with a loading bolt fabricated from the same material as the C-ring. The loading bolt threaded directly into one side of the C-ring, eliminating the need for the loading nut. The C-rings and loading bolt were machined from archived material removed from Hanford's 241-AP tank farm following tank fabrication and stress relief annealing in 1985. The C-rings were approximately 2.5×10^{-2} m in diameter, 2.5×10^{-2} m in width, and 6.4×10^{-3} m in wall thickness giving a surface area (including loading nut) of approximately 4.7×10^{-3} m^2. The test solution was brought up to 97°C and the electrodes were inserted. As with the previous tests, current and potential fluctuations from the C-rings were random in nature, slowly decreasing in frequency and magnitude over the first 10 h of exposure. Current and potential fluctuations over the first 10 h of testing were characteristic of uniform corrosion in a passivating system with a small amount shallow pitting occurring just after immersion. Electrodes were not removed until the conclusion of testing.

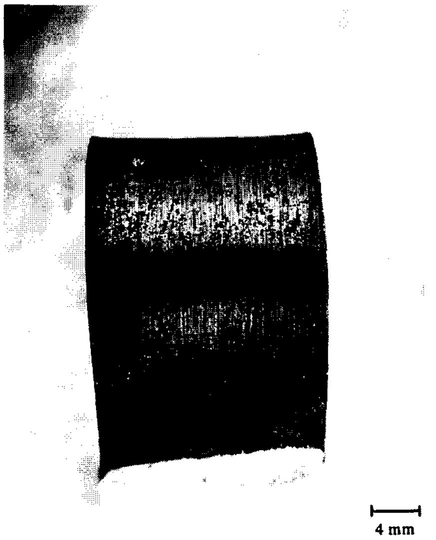

Fig. 9. ASTM A516-Grade 60 U-bend – 46 h exposure, 4.0 M NH_4NO_3, 97°C.

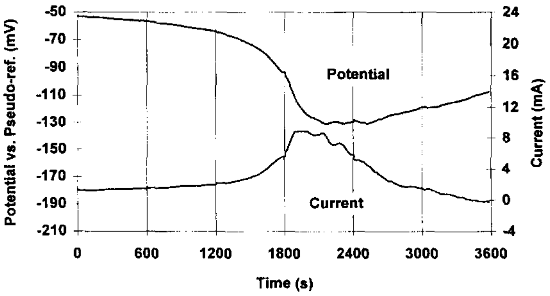

Fig. 10. SCC Propagation – ASTM A537-Class 1 C-ring, 4.0 M NH_4NO_3 at 97°C, 1 h of data taken after 24 h of exposure.

At approximately 10 h into the exposure, sharp 75–100 mV drops in working electrode potential accompanied by 8–10 mA current bursts began to occur. An hour of data collected after 24 h of exposure is shown in Fig. 10. An hour of data collected after 35 h of exposure is shown in Fig. 11. The sharp simultaneous spikes in current and voltage persisted for a total of 120 h. Approximately 15 transients similar to those shown in Figs. 10 and 11 were collected prior to test termination. The effects of these transients on the standard deviation of current over the course of testing are evident in Fig. 12. The test was terminated after 143 h. Upon removal of the electrodes, it was observed that a primary intergranular crack had propa-

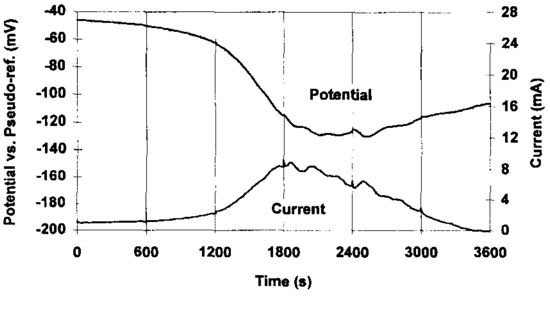

Fig. 11. SCC Propagation – ASTM A537-Class 1 C-ring, 4.0 M NH_4NO_3 at 97°C, 1 h of data taken after 35 h of exposure.

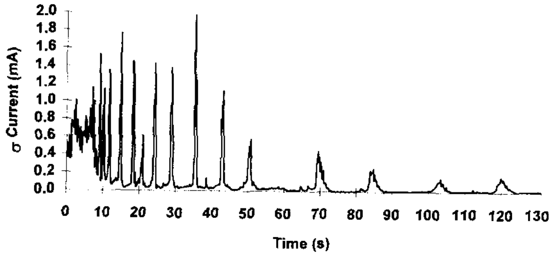

Fig. 12. Standard deviation of current during SCC of ASTM A537-Class 1 exposed to 4.0 M NH_4NO_3 at 97°C for 130 h: SCC propagation in working electrode starts at ~ 10 h.

gated across the width of the electrode ($\sim 2.5 \times 10^{-2}$ m) and from approximately 2–4 mm in depth as shown in Fig. 13. The remaining surfaces of all three electrodes were smooth and covered with a dark powdery oxide layer.

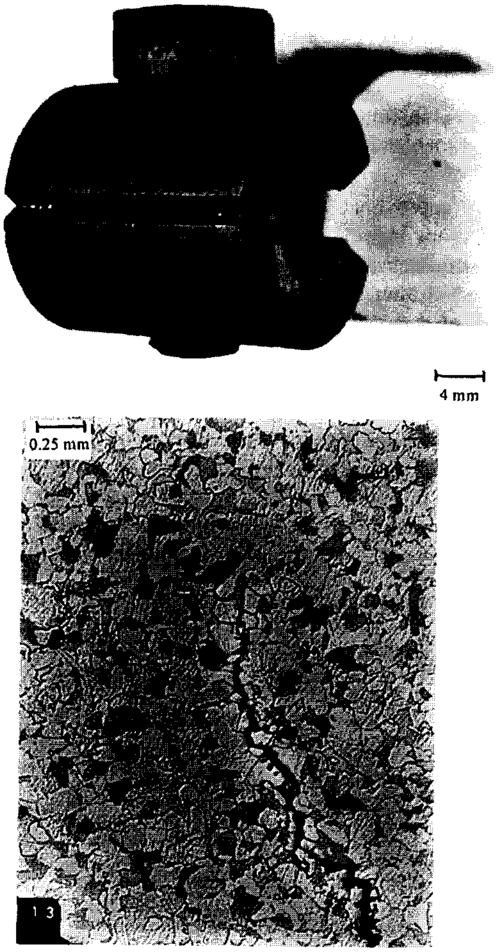

Fig. 13. ASTM A537-Class 1 C-ring – 143 h exposure.

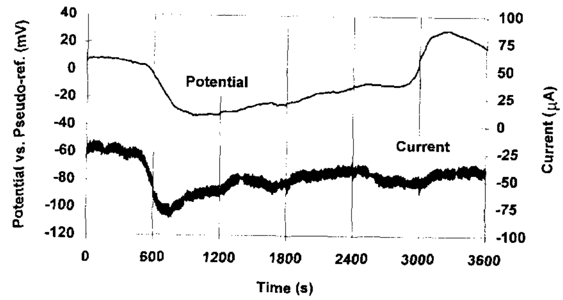

Fig. 14. SCC propagation, no SCC signal recorded – ASTM A216-C compact tension specimen, 5.0 M $NaNO_3$ at 97°C, 1 h of data taken after 31 h of exposure.

4.3. IGSCC of an ASTM A216-C compact tension (CT) specimen in 5.0 M sodium nitrate at 97°C

Following the work with U-bends, there was an attempt to monitor crack propagation over a longer period of time than that permitted by U-bend specimens. An ASTM A216-C 1T pre-cracked CT specimen loaded and coated with Miccrotex [3] over all surface areas except the pre-crack mouth was prepared for this purpose. Counter and pseudo-reference electrodes had similar surface areas as the pre-crack mouth and were also made of ASTM A216-C steel. A 5.0 M sodium nitrate solution held at 97°C was used for the test environment. Electrodes were immersed and monitored for approximately 165 h. An hour of data collected after 31 h of immersion is shown in Fig. 14. Data similar to Fig. 14 were collected throughout the remainder

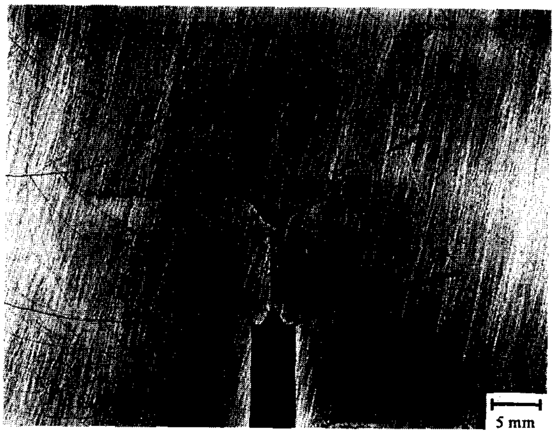

Fig. 15. ASTM A216-C compact tension electrode crack detail – 165 h exposure, 5.0 M $NaNO_3$, 97°C.

---

[3] Miccrotex is a trademark of Tolber Division Inc., Hope, Arkansas.

of the test. In general, nearly all of the data collected during this exposure indicated only uniform corrosion during passivation. Testing was terminated after 165 h. Upon removal of the specimens, it was observed that multiple branched intergranular cracks had propagated deeply (~ 17 mm) into the stressed portion of the electrode. At the conclusion of testing, all uncoated surfaces of the electrodes were slightly oxidized. The coating material had delaminated from the edges of the exposed surface on the working electrode. The working electrode following testing is shown in Fig. 15 (coating completely removed for clarity).

5. Discussion

5.1. Uniform corrosion

Small random fluctuations of current and potential have been shown to be characteristic of uniform corrosion [20–25]. Current and potential fluctuations produced by uniform corrosion are the result of random shifts back and forth between anodically and cathodically dominated behavior of the counter and the working electrodes. The reduction in frequency and magnitude of current and potential fluctuations over time is assumed to result from a reduction in electrochemical activity due to the development of a stable, passive layer on the electrodes. Tests using 4.0 M ammonium nitrate solutions at 97°C were performed using both ASTM A516-Grade 55 and A537-Class 1 material. Both materials exhibited highly active surfaces upon exposure to the ammonium nitrate solution. This period of high activity typically persisted for 20–30 h and was marked by large, random fluctuations in current and potential. Upon electrode removal after ~ 24 h of exposure, the ASTM A516-Grade 55 electrodes were found to be covered with shallow pits similar to those shown in Fig. 3. The ASTM A537-Class 1 electrodes were smooth and lightly oxidized with no signs of pitting attack. Close inspection of unused electrodes revealed that the ASTM A516-Grade 55 pins used for these tests suffered micropitting during the manufacturer's electropolishing process, prior to their exposure to ammonium nitrate test solutions. These micropits, when exposed to the ammonium nitrate test solution, grew wider and deeper to generate an electrode surface similar to that shown in Fig. 3. Electrodes which were hand polished to remove the micropits from the electropolishing process generated uniformly corroded, smooth, oxidized surfaces upon exposure to ammonium nitrate.

The fluctuations of current and potential recorded from ASTM A537-Class 1 in the more passive simulated inhibited waste solution were also typical of uniform corrosion, but approximately two orders of magnitude smaller than those recorded from the same material exposed to 4.0 ammonium nitrate. Unlike the ammonium nitrate solutions, electrodes exposed to the simulated waste showed no initial period of high electrochemical activity since the electrodes passivated rapidly in the high pH solution. This behavior was typical of all passivating systems that underwent uniform corrosion; more passive systems produced lower corrosion rates, lower mean currents, and smaller fluctuations in current.

5.2. Stress corrosion cracking

An active-path dissolution model has been proposed by many researchers to explain IGSCC in steel/nitrate systems [29]. Active-path dissolution processes result from compositional differences between grain boundary and grain body material. These differences cause grain boundaries to become anodic with respect to grain bodies when mild steels are exposed to boiling ammonium nitrate. Cracks advance primarily by nearly continuous, preferential anodic dissolution of the grain boundaries. In all tests that utilized a stressed working electrode, mean current was always positive and mean potentials were negative until late in the test period. These results support the concept of a nearly continuous anodic process occurring at the crack tip on the working electrode. Mean current and mean potential recorded in tests using unstressed electrodes fluctuated around zero throughout the electrode exposure. It has been reported that cracks propagating steadily by an active path dissolution process can periodically jump via mechanical fracture of the grain boundary surface [32]. The bare metal exposed by this process is highly anodic relative to the otherwise oxidized electrode surface and quickly undergoes anodic dissolution. This results in a sudden increase in current increase and simultaneous drop in potential. The 10–15 large current and potential transients recorded in each of the SCC tests using U-bends or C-rings are hypothesized to be the result of this type of mechanical fracture.

The most sensitive statistical parameter to the onset of SCC is the standard deviation of current. Mean current, standard deviation of potential, and mean potential can also be effectively used to identify the onset of SCC. Since current rises sharply when cracks propagate (via grain boundary fracture), the standard deviation of current is much higher for data files that capture large crack propagation events than for data files collected when cracks are not propagating. When the standard deviation of current for each data file is plotted against elapsed time of testing, data files that capture crack propagation events can be easily identified by sharp positive spikes. This effect is illustrated clearly in Fig. 12. The standard deviation of potential, mean current, and mean potential behave analogously. Spikes similar to those in Fig. 12 were not recorded from electrodes that suffered only uniform corrosion.

It is worth noting that current and voltage signal behavior described for U-bends and C-rings was not supported by the ASTM A216-C compact tension electrode. Despite

Table 2
Crack propagation rates in selected steel/nitrate systems

Test description	Crack depth (m)	Cracking time (h)	Cracking rate (m/s)
ASTM A516-Grade 60 U-bend, 4.0 M NH_4NO_3, 97°C	1.3×10^{-3}	27	1×10^{-8}
ASTM A537-Class 1 C-ring, 4.0 M NH_4NO_3, 97°C	2.0×10^{-3}	110	5×10^{-9}
ASTM A216-C Compact Tension, 5.0 M $NaNO_3$, 97°C	8.6×10^{-3}	140	2×10^{-8}

the propagation of several large cracks into the working electrode, there were no obvious SCC transients in the raw data files. Hundreds of raw data files were examined over the course of the test on the compact tension specimen. Generally, the raw data showed characteristics of uniform corrosion. There were periods in which the current and potential data were cyclic in nature, but no corrosion current or potential transients indicating SCC initiation or propagation were detected despite significant crack growth. The poor sensitivity and lack of SCC transients in the raw data from the coated compact tension electrode is likely the result of the large surface area of the crack face compounded by the delamination of the coating around the unpainted surface area. Crack advance is only recorded when a detectable number of electrons flow through the ZRA from the working electrode to the counter electrode. Most of the electrons released by anodic dissolution at the crack tip in the compact tension specimen were likely consumed in cathodic reactions in the crack mouth or elsewhere on the large oxidized surface of the working electrode. Since most of the electrochemical events were confined to one electrode (compact tension), very little signal could be recorded. Working electrodes for use in SCC monitoring must restrict the increase in crack-face surface area associated with crack advance by limiting possible crack propagation depth.

At the conclusion of testing, crack advance rates were estimated for each test. Crack advance rates for U-bends and C-rings were estimated from duration of SCC EN signal generation and post-test crack depth. Crack advance rate for the compact tension specimen was estimated from length of exposure and periodic crack depth measurements. Crack advance rates determined by both methods compared favorably with previously published results [30]. Results are shown in Table 2.

6. Conclusions

(1) The measurement of EN for use as a corrosion monitoring technique was shown to be capable of detecting and distinguishing between uniform corrosion and SCC in mild steel/nitrate systems when proper electrode geometries are used.

(2) Uniform corrosion is characterized by random fluctuations in current and potential in the raw data caused by random shifts between anodically and cathodically dominated behavior of the electrodes. In passivating systems, the fluctuations tended to decrease in frequency and magnitude over time as the surfaces of the electrodes passivated. In general, lower corrosion rates were associated with lower mean currents and smaller fluctuations in current.

(3) Crack advance is characterized by sharp, periodic drops in potential occurring simultaneously with positively directed bursts of current in the raw data. Between these events, mean current is positive and mean potential is negative, suggesting a nearly continuous anodic process occurring at the crack tip on the working electrode. These results support the active path dissolution model proposed by many to explain crack advance in mild steel/nitrate systems.

Acknowledgements

This work represents the cooperative efforts of many people and organizations from diverse backgrounds and ranges of interest. The tests were conducted over the course of two years by personnel from the Materials and Corrosion Engineering group within Lockheed Martin Hanford Corporation, the Materials Development group of the Structural Materials Research Section at Pacific Northwest National Laboratory, and the Corrosion Science and Technology Group at Oak Ridge National Laboratory. The technical support of Mr. Phil Ohl, Mr. James Nelson, Mr. Ivar Husa, and Dr. Ramamohan Anantatmula of Lockheed Martin Hanford Corporation, Dr. Dane Wilson of Oak Ridge National Laboratory, Dr. Kevin Lawson of The Mentor_1 Group, and Mr. Matt Rhodes of Gamry Instruments, Incorporated is also gratefully acknowledged.

References

[1] P.C. Ohl, J.D. Thomson and F.R. Vollert, in: CORROSION/94, paper No. 142 (National Association of Corrosion Engineers, Houston, TX, 1994).

[2] D.C. Lini, Compilation of Hanford Corrosion Studies, Atlantic Richfield Hanford Company Report, ARH-ST-111, UC-70 (1975).

[3] J.R. Divine, W.M. Bowen, D.B. Mackey, D.J. Bates and K.H. Pool, Prediction Equations for Corrosion Rates of A537 and A516 Steels in Double Shell Slurry, Future PUREX, and

Hanford Facilities Wastes, Pacific Northwest Laboratory Report, PNL-5488 (1985).

[4] W.C Carlos, in: CORROSION/95, paper No. 449 (National Association of Corrosion Engineers, Houston, TX, 1995).

[5] J.L. Nelson, in: CORROSION/95, paper No. 440 (National Association of Corrosion Engineers, Houston, TX, 1995).

[6] R.K. Shukla, A.J. Perkins, P.M. Bourgeois, R.J. Jaramins, W.G. Secen and, D.J. Stroud, in: CORROSION/94, paper No. 121 (National Association of Corrosion Engineers, Houston, TX, 1994).

[7] J.I. Mickalonis, R.J. Jacko, G.P. Quirk and D.A. Eden, in: Proc. First Int. Symposium on Electrochemical Noise Measurements for Corrosion Applications, ASTM STP 1277, eds. J.R. Kearns, J.R. Scully, P.R. Roberge, D.L. Reichert and J.L. Dawson (American Society for Testing and Materials, Philadelphia, PA, 1996) p. 201.

[8] T. Haygard and J.R. Williams, Trans. Faraday Soc. 57 (1961) 2288.

[9] P. Bindra et al., Discuss. Faraday Soc. 56 (1974) 189.

[10] M. Fleischmann et al., Surf. Sci. 100&101 (1980) 583.

[11] G.J. Bignold and M. Fleischmann, Electrochem. Acta 19 (1974) 363.

[12] E. Budevski et al., Electrochem. Acta 28 (1983) 925.

[13] G. Blanc et al., Electrochem. Acta 23 (1978) 337.

[14] K. Hladky and J.L. Dawson, Corros. Sci. 23 (1982) 231.

[15] D.A. Eden, J.L. Dawson and D.G. John, UK patent application 861158, May 1986, US patent 5139627.

[16] K. Hladky, European patent 084404A3, US patent 455709, Canadian patent 418938.

[17] U. Bertocci, in: CORROSION/89, paper No. 24 (National Association of Corrosion Engineers, Houston, TX, 1989).

[18] J.L. Dawson, D.M. Farrell, P.J. Aylott and K. Hladky, in: CORROSION/89, paper No. 31 (National Association of Corrosion Engineers, Houston, TX, 1989).

[19] D.A. Eden, A.N. Rothwell and J.L. Dawson, in: CORROSION/91, paper No. 444 (National Association of Corrosion Engineers, Houston, TX, 1991).

[20] D.M. Farrell, Ind. Corros. 9 (1991) 7.

[21] A.N. Rothwell, T.G. Walsh and W.M. Cox, in: CORROSION/91, paper No. 170 (National Association of Corrosion Engineers, Houston, TX, 1991).

[22] G.L. Edgemon and G.E.C. Bell, Technical Basis for Electrochemical Noise Based Corrosion Monitoring of Underground Nuclear Waste Storage Tanks, Westinghouse Hanford Company Report WHC-SD-WM-TI-772 (1996).

[23] D.M. Farrell, W.M. Cox and D. Gearey, Multi-System Corrosion Monitoring in a Cyclic Reheat Test Facility; Phase 1, Electric Power Research Institute Report CS-5776 (1988).

[24] D.M. Farrell, W.M. Cox and D. Gearey, Multi-System Corrosion Monitoring in FGD Systems; Phase 2, Electric Power Research Institute Report CS-5734 (1988).

[25] B.C. Syrett and W.M. Cox, in: Proc. 1st Int. Symp. on Electrochemical Noise Measurements for Corrosion Applications, ASTM STP 1277, eds. J.R. Kearns, J.R. Scully, P.R. Roberge, D.L. Reichert and J.L. Dawson (American Society for Testing and Materials, Philadelphia, PA, 1996) p. 173.

[26] C.A. Lotto and R.A. Cottis, Corrosion 45 (1989) 136.

[27] P.E. Doherty, M.J. Psaila-Dombrowski, S.L. Harper and W.G. Schneider, in: Proc. 1st Int. Symp. on Electrochemical Noise Measurements for Corrosion Applications, ASTM STP 1277, eds. J.R. Kearns, J.R. Scully, P.R. Roberge, D.L. Reichert and J.L. Dawson (American Society for Testing and Materials, Philadelphia, PA, 1996) p. 288.

[28] L. Beaunier, J. Frydman, C. Gabrielli, F. Huet and M. Keddam, in: Proc. 1st Int. Symp. on Electrochemical Noise Measurements for Corrosion Applications, ASTM STP 1277, eds. J.R. Kearns, J.R. Scully, P.R. Roberge, D.L. Reichert and J.L. Dawson (American Society for Testing and Materials, Philadelphia, PA, 1996) p. 114.

[29] H.L. Logan, The Stress Corrosion of Metals (Wiley, New York, 1966).

[30] J.A. Donovan, in: Environmental Degradation of Engineering Materials (Virginia Tech Printing Department, Blacksburg, VA, 1977) p. 185.

[31] R.S. Ondrejcin, S.P. Rideout and J.A. Donovan, Nucl. Technol. 44 (1979) 297.

[32] R.H. Jones and R.E. Ricker, Stress Corrosion Cracking, ed. R.H. Jones (ASM International, Materials Park, OH, 1992).