An Investigation of the Mechanism of IGA/SCC of Alloy 600 in Corrosion Accelerating Heated Crevice Environments

Topical Report: Phase I (08/18/1999 - 08/31/2000)
Prime Contract: DE-FG03-99SF21921

Prepared for:

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November 27, 2000

In reply please refer to G.O. 71165

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Attention: Katherine Woo

Subject: Topical Report - Progress Report Phase 1 Activities
Investigation of the Mechanism of IGA/SCC of Alloy 600 in
Corrosion Accelerating Heated Crevice Environments
For the period 8/18/99 through 8/31/2000
Prime Contract No. DE-FG03-99SF21921
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Enclosed is the subject report.

Sincerely,
ROCKWELL SCIENCE CENTER, LLC

Jesse Lumsden
Principal Investigator

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An Investigation of the Mechanism of IGA/SCC of Alloy 600 in Corrosion Accelerating Heated Crevice Environments

Nuclear Energy Research Initiative (NERI) Program
DE-FG03-99SF21921

Topical Report: Phase 1 Activities (08/18/1999 – 08/31/2000)

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Introduction

The crevice formed by the tube/tube support plate (T/TSP) intersection in a pressurized water reactor (PWR) steam generator is a concentration site for nonvolatile impurities (referred to as hideout) in the steam generator water. The restricted mass transport in the small crevice volume prevents the species, which concentrate by a thermal/hydraulic mechanism during the generation of steam, from quickly dispersing into the bulk water. The presence of a porous scale corrosion product on the surface of the tube and deposits of corrosion products in the crevice further restrict mass transport.

The concentrated solutions and deposits in T/TSP crevices have been correlated with several forms of corrosion on the OD of steam generator tubes including intergranular attack/stress corrosion cracking (IGA/SCC), pitting, and wastage. The rate and type of corrosion are dependent on pH, specific anions, and the electrochemical potential. Careful water chemistry control and other remedial measures have essentially stopped all forms of secondary side corrosion except IGA/SCC.

Crevice chemistries in an operating steam generator cannot be measured directly because of their inaccessibility. In practice, computer codes (MULTEQ, Molar Ratio Index, etc.) based upon hypothesized chemical reactions and thermal hydraulic mechanisms are used to predict crevice chemistry. The Rockwell program provides an experimental base to benchmark crevice chemistry models and to benchmark crevice chemistry control measures designed to mitigate IGA/SCC.

The objective of this program is to develop an understanding of the corrosion accelerating mechanisms, particularly IGA/SCC, in steam generator crevices. The important variables will be identified, including the relationship between bulk water chemistry and corrosion accelerating chemistries in a crevice. An important result will be the identification of water chemistry control measures needed to mitigate secondary side IGA/SCC in steam generator tubes. The approach uses an instrumented heated crevice, which is a replica of a PWR steam generator T/TSP crevice. While the system is operating at simulated steam generator thermal conditions, measurements can be made of the chemical, electrochemical, and thermal conditions in the crevice. Damage to the tube due to IGA/SCC and other corrosion processes will be monitored using electrochemical noise.

PHASE 1 PROGRESS

Background

In Phase 1 we completed the construction of the instrumented heated crevice used in this program. Topical Report-1 gives a detailed description of this apparatus. Also, during Phase 1 an electrochemical noise (EN) system was set up. EN measurements were made using Alloy 600 C-rings in a static autoclave and on an Alloy 600 pressurized tube in the instrumented heated crevice. These results have established baseline measurements for reference conditions and will be described here.

The inaccessibility of the T/TSP crevice in an operating steam generator has always been an issue in evaluating aggressive crevice chemistries and assessing damage to the tube caused by corrosion. The electrochemical sensors in our laboratory replica of a T/TSP crevice and the capability of solution extraction from this geometry enables us to evaluate crevice chemistry during simulated steam generator thermal conditions. EN is being developed for *in situ* monitoring of the initiation and propagation of IGA/SCC.

The EN technique is based on the electrochemical nature of corrosion processes and the distinctive nature of EN signatures for all corrosion processes. EN signatures are seemingly random low-frequency fluctuations in electrochemical potential and current, which occur at the electrode surface during corrosion. The EN signature from SCC of Alloy 600 results from the creation of new surface area, when a crack is initiated or advances. When a crack initiates or propagates, there is a transient surge in current associated with the oxidation processes of dissolution and film formation on the new surface exposed to the aqueous solution. Most of the current surge is from dissolution, which decreases rapidly as new oxide film is formed on the newly created surface.

All EN analysis of the various corrosion processes, including SCC, employ the same basic setup and analysis of results. Typically, an EN experiment has two nominally identical electrodes coupled together via a zero-resistance-ammeter (ZRA) without the application of an external signal. Since the two electrodes are shorted through the ZRA, this insures that they are at the same potential. The electrochemical potential noise of the couple is monitored as a fluctuation of potential with respect to either a reference electrode, or a pseudo reference electrode. The time records for the current and potential allow evaluation of a number of statistical parameters for the respective signals. This analysis permits the assessment of the mechanism and severity of the corrosion processes occurring. The electrochemical current noise may also be measured as the current to a single working electrode that is held at a fixed potential.

Caustic or highly alkaline conditions in steam generator crevices appear to be the most common cause of IGA/SCC of Alloy 600 tubes in plants (1). Several laboratories have reproduced this type of cracking using static autoclaves, and have shown that caustic alone is sufficient to cause IGA/SCC in Alloy 600 steam generator tubes. Thus, a 50% NaOH solution was chosen as a reference environment for static autoclave work. Feedwater with 40 ppm NaOH was chosen as the reference condition for the heated crevice work. For the static autoclave tests, EN was measured from C-ring specimens. In the heated crevice experiments, EN was measured from the pressurized steam generator tube.

Laboratory results show that IGA/SCC susceptibility of Alloy 600 exposed to a caustic environment depends on the electrochemical potential (2-5). Figure 1 shows the potential dependence. Susceptibility to SCC lies in the potential range of from approximately 150 mV to approximately 300 mV with respect to a Ni wire pseudo reference electrode. For this reason, the EN measurements for SCC were made on C-rings polarized at 200 mV.

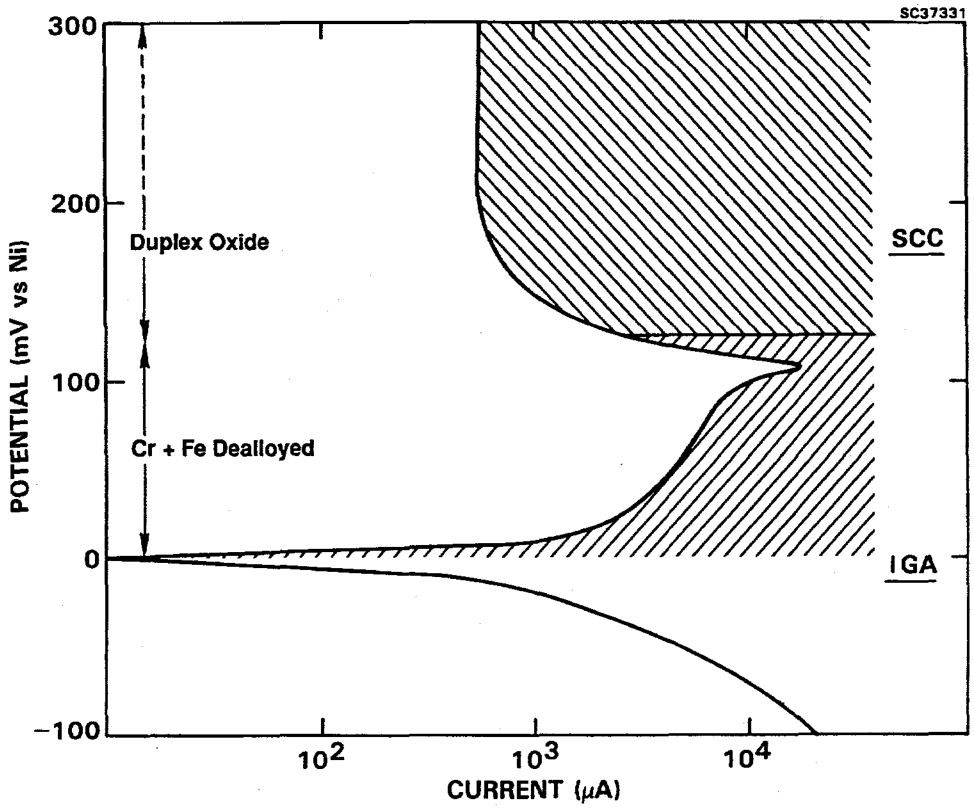


Figure 1. Potential bands where IGA and SCC (SCC not observed above 300 mV) occur in a caustic solution (2-4).

EXPERIMENTAL

The C-ring specimens used in the static autoclave tests were prepared according to ASTM G38-73 and were strained to a constant deflection corresponding to a maximum stress at the apex of 150% of yield calculated according to

$$\Delta = s\ p\ D^2/4EtZ$$

where s is the desired stress, Δ is the change of OD giving the desired stress, D is the mean diameter (OD − t), t is the wall thickness, E is the modulus, and Z is a correction factor for curved beams.

Figure 2 is a schematic of the autoclave/electrochemical noise system. Measurements were conducted in 750 ml nickel-lined, Alloy 718 autoclaves. The ends of the screws used to apply stress to the C-ring specimens were bolted to Alloy 600 rods mounted on the autoclave head by fittings that electrically isolated the rods from the autoclave. A cylindrical nickel counter electrode, electrically isolated from the autoclave, completely surrounded the specimens. A nickel wire reference electrode was used. It has been shown (5` `) that a Ni wire in a high temperature caustic environment with a hydrogen cover gas is a hydrogen electrode. Although the Ni reference wire may become coated with metal oxides, which precipitate from solution, the coatings are porous and are not electrochemically active; thus, the reference potential remains fixed by the hydrogen fugacity and the pH.

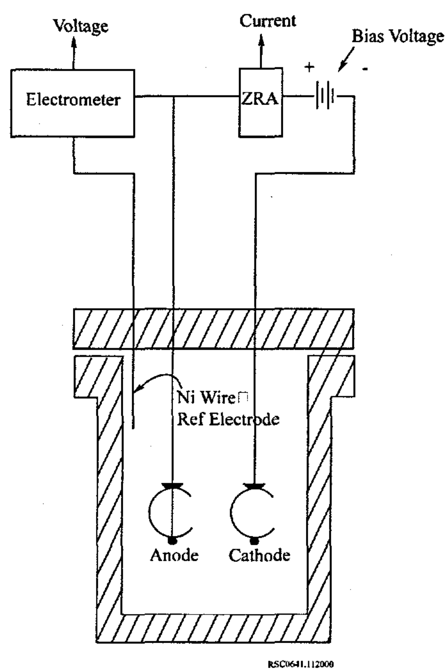


Figure 1. Schematic of static autoclave configuration.

In each test, the quantity of electrolyte added was adjusted so that at test temperature the electrolyte level was at least 5 mm above the top of the specimens. The cover gas was 5% hydrogen/95% argon. Before heating, the solution was deoxygenated in the autoclave by three pressurizing/aspirating cycles from 1.4 to 13.6 MPa (200 psia to 2000 psia). Each pressurization was held for 30 min followed by a slow release of the gas. Following the last aspiration, heating was begun with a 1.4 MPa (200 psia) overpressure to maintain a stable immersion level. This gave a hydrogen pressure of 0.07 MPa in equilibrium with the Ni wire "hydrogen electrode".

Measurements of current noise are made between two nominally identical C-rings, one of which was at open circuit and the other was polarized at 150 mV or 200 mV. Measurements were made with one C-ring stressed at above yield at the apex and the other was not stressed. The current noise was measured by connecting the two C-rings with a zero resistance ammeter using a Gamry ESA400 data acquisition unit (Figure 2). For comparison, the identical experiment was performed, in which both C-rings had no applied stress.

Figure 3 is a schematic of the heated crevice used to measure SCC in Alloy 600 steam generator tubes under heat flux conditions similar to those found in nuclear steam generators. A full description of this system and its capabilities are in Topical Report #1. EN measurements of SCC in the Alloy 600 steam generator tube in the heated crevice were made with the tube pressurized at 2300 psi. The pressure in the autoclave was adjusted so that the boiling point of the bulk water was 280°C. The tube heater was operated with a superheat of 45°C. Feedwater having 40 ppm NaOH was circulated through the autoclave at 2 liters/min. The current noise was monitored between the Alloy 600 tube and an Alloy 600 ring used to form the simulated T/TSP crevice. Potential noise was monitored between the tube and a Ni rod pseudo reference electrode, which was inserted into the crevice.

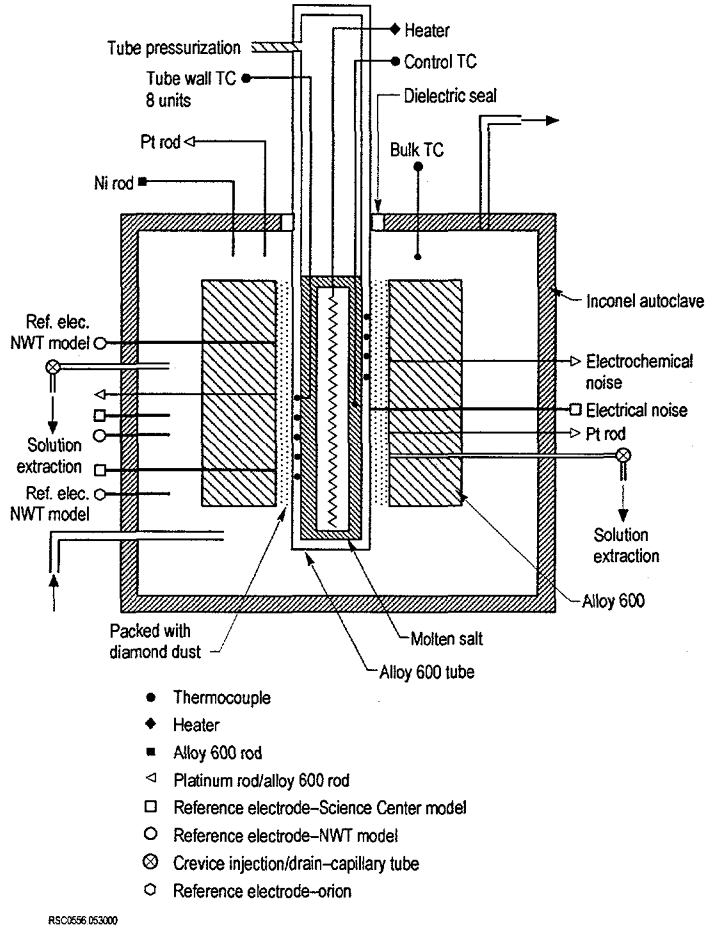


Figure 3. Schematic of the heated crevice configuration.

RESULTS

Figure 4 shows the current between the C-ring couple in which neither C-ring had an applied stress. One C-ring in the couple had an applied potential of 150 mV relative to the Ni wire pseudo reference electrode. The current data shown was collected over a 35 hour period and had a mean value of zero. The maximum drift was ± 0.5 mA. Figure 5 has an expanded current axis and shows the current data over a 1000 second period between 14 and 15 hours in Figure 4. This figure shows that the ac signal on the current between the two C-rings with no stress is approximately 0.05 mA.

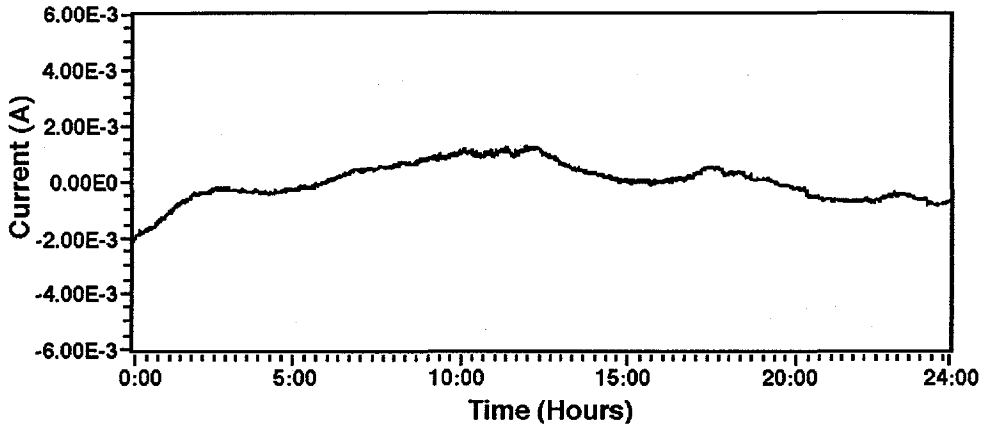


Figure 4. Current noise from a couple formed by an Alloy 600 C-ring, neither of which has an applied stress. The environment was 50% NaOH at 320°C.

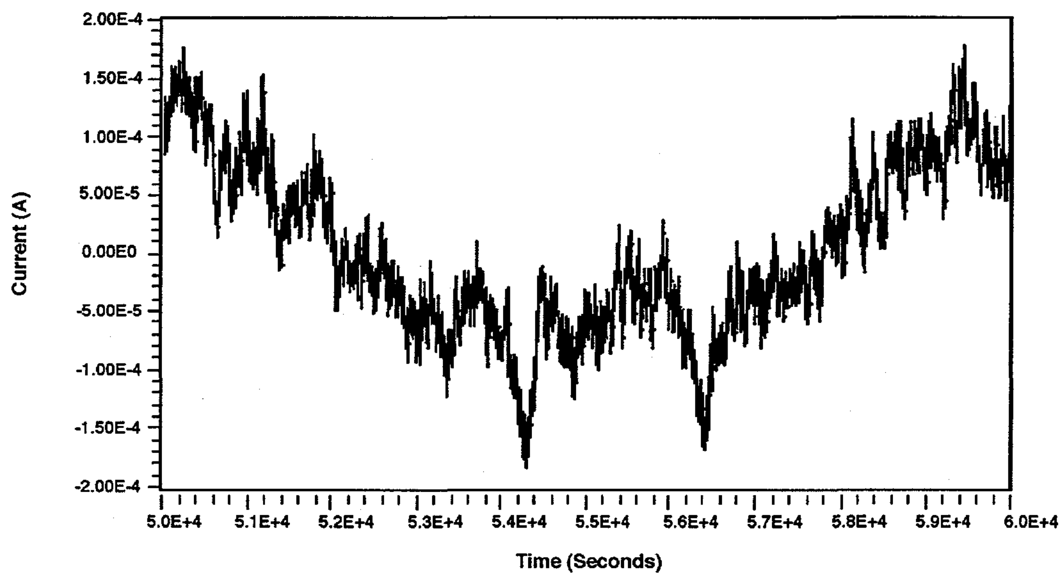


Figure 5. A typical 1000 second time interval in the current noise from a couple formed by an Alloy 600 C-ring, neither of which has an applied stress. Note that the y-axis has been expanded 50X relative to that in Figure 4.

Figure 6 shows the current between the C-rings in a couple in which one C-ring had an applied stress of 150% yield. The C-ring with an applied stress was polarized 150 mV. Clearly the couple with the stressed C-ring has regions where the peak-to-peak current transients exceed those from the couple in which neither C-ring had an applied stress by almost two orders of magnitude. The four specimens of the two couples were contained in the same autoclave. When the C-rings were examined after the experiment, a through-wall, intergranular crack was found in the specimen that had the applied stress. There were no cracks in the specimens, which were not stressed. An examination of the data from the couple with the stressed C-ring suggests that crack growth was discontinuous and occurred during four 2 to 5 hour intervals over the two day test period. An expanded time scale of two regions of hypothesized rapid crack growth shows that the current during the 3.5-hour time period shown is rich in structure. An examination of the C-rings after the tests showed that all of the C-ring specimens with applied stress had through-wall cracks at the apex.

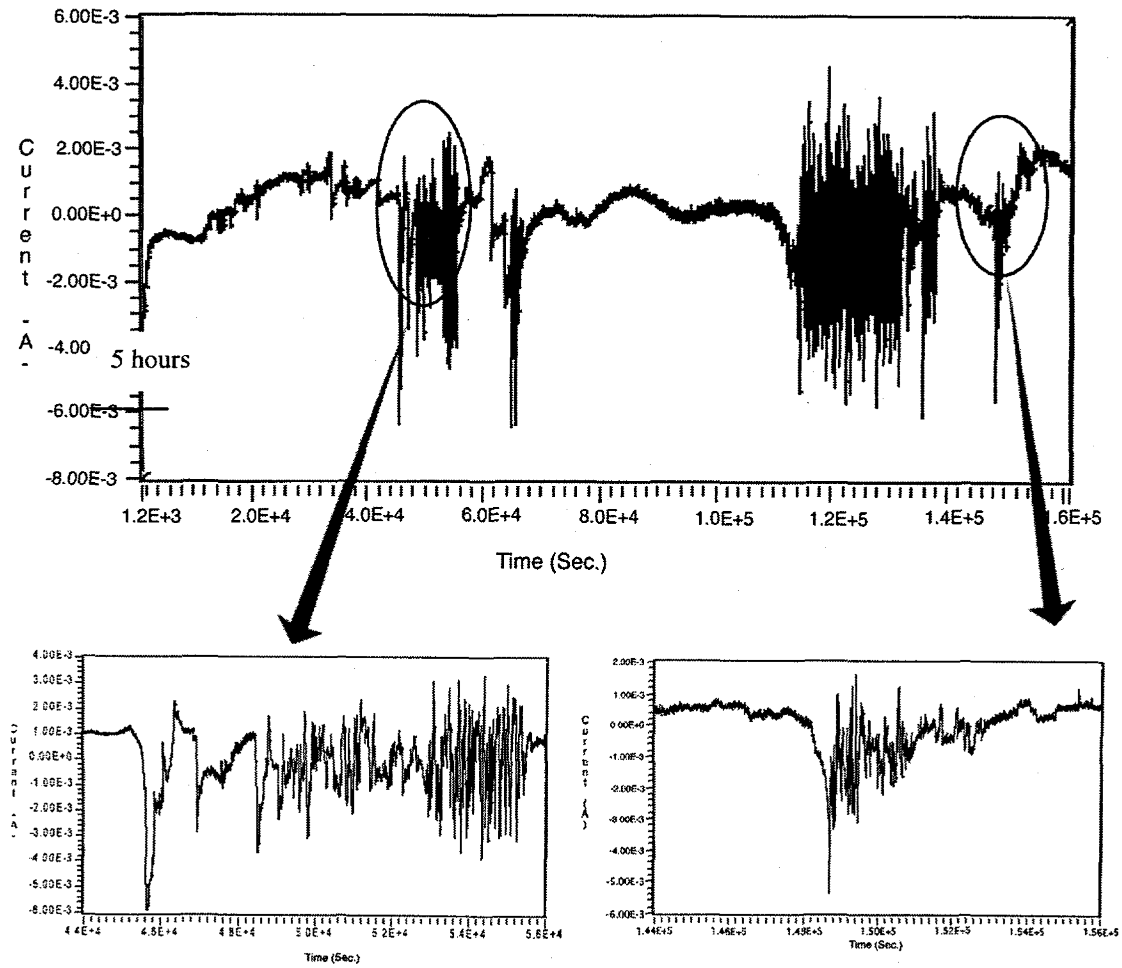
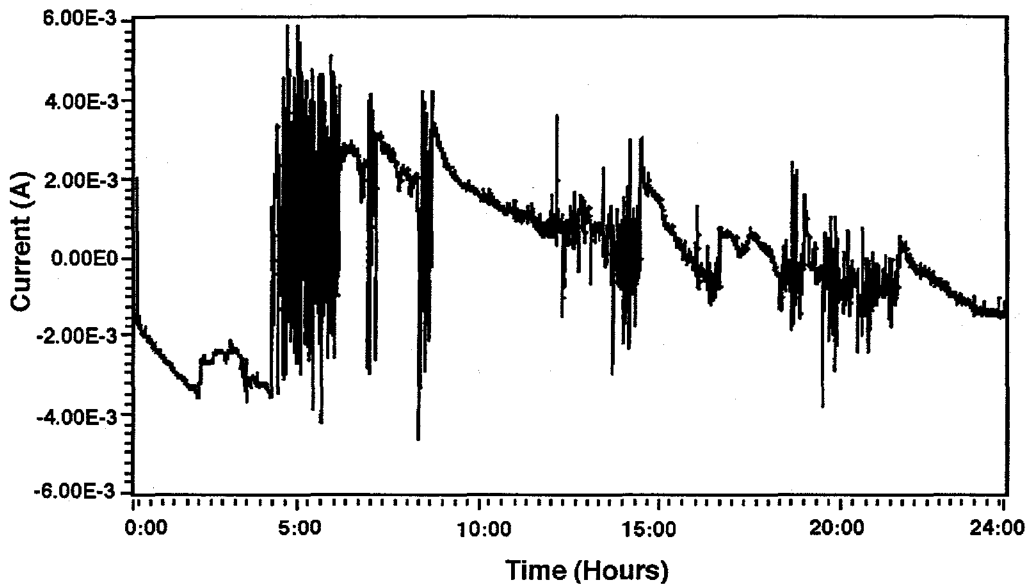
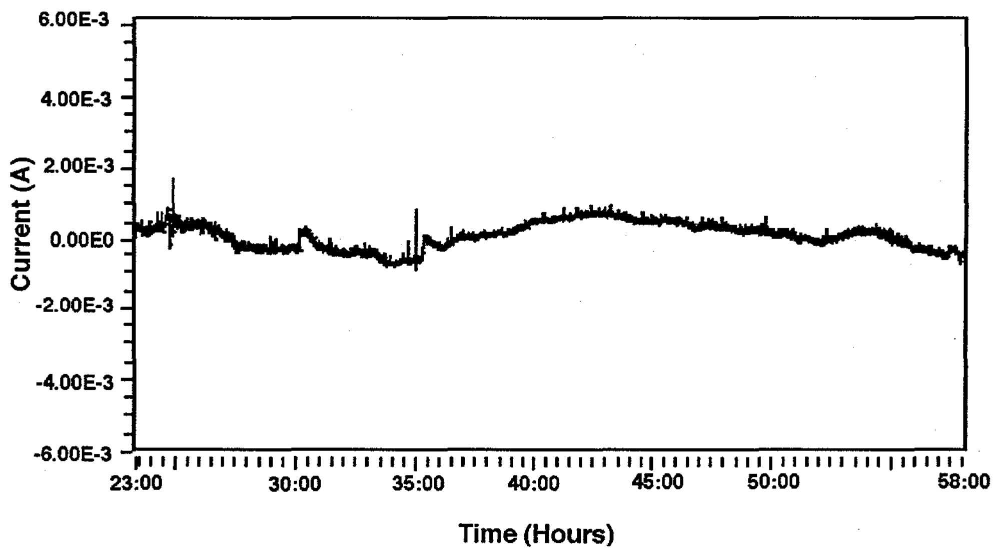


Figure 6. Current noise from a couple formed by an Alloy 600 C-ring stressed at 150% yield and one with no applied stress. The environment was 50% NaOH at 320°C.

Figure 7 is the current data from a C-ring couple in which one specimen had no stress and the second had an applied stress of 160% yield and was polarized 200 mV. The current data has fluctuations much like those shown in Figure 6 for the specimen stressed at 150% and polarized at 150 mV. However, all of the large fluctuations stop after approximately 22 hours. The data taken after 22 hours resemble that from the couple in which neither specimen is stressed. An inspection of the stressed C-ring after the test found a through wall crack at the apex. An independent test of a C-ring stressed at 160% of yield and polarized at 200 mV showed that the crack went through wall within a 24-hour period.



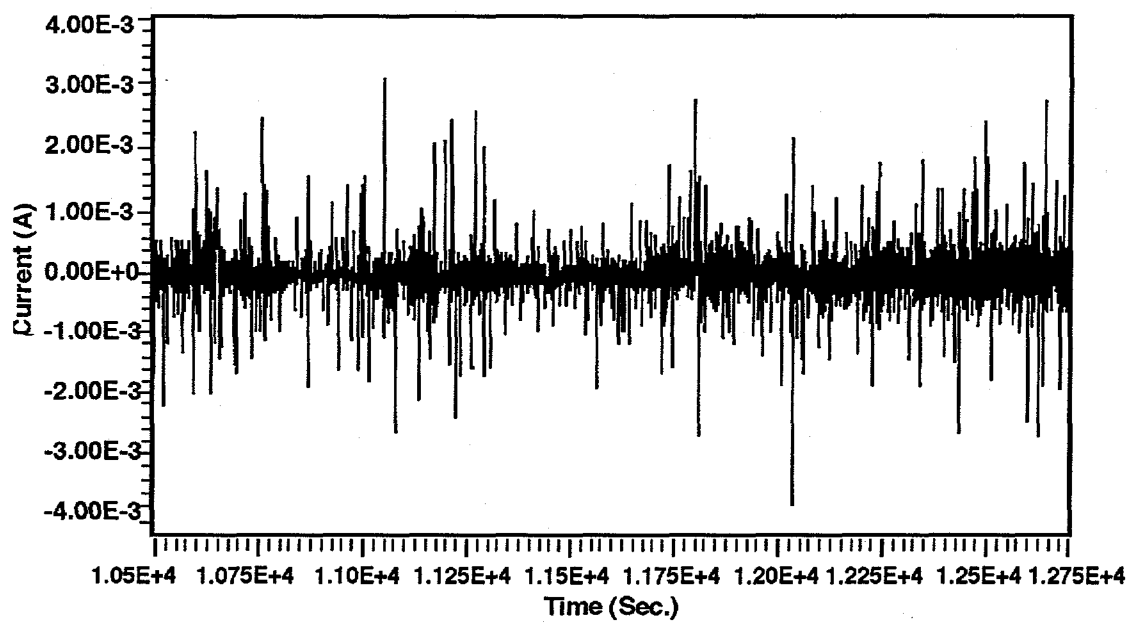
a)



b)

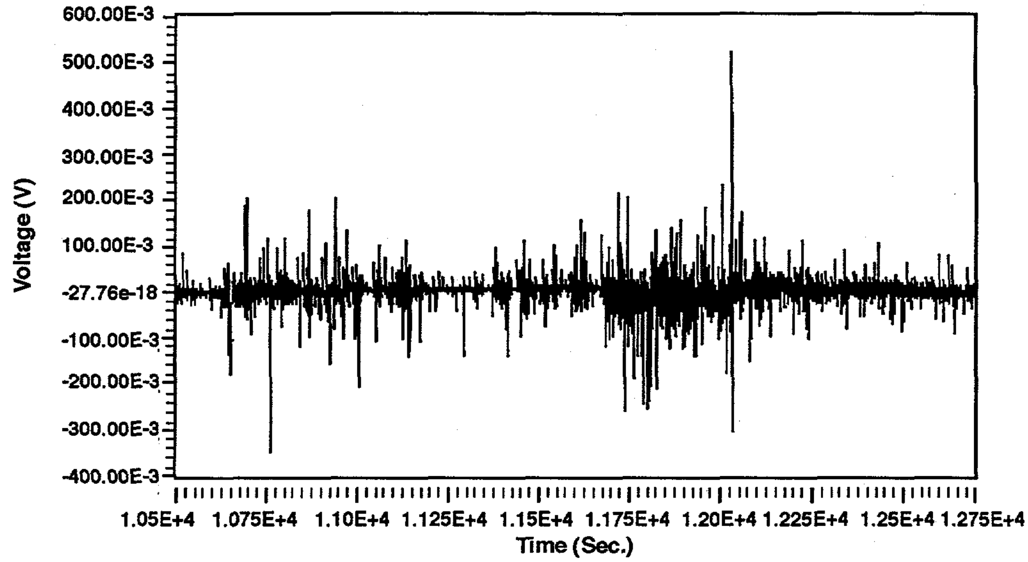
Figure 7. Current noise from a couple formed by an Alloy 600 C-ring stressed at 160% yield and one with no applied stress a) during the first 24 hours of the test and b) during the second 24 hours of the test. The environment was 50% NaOH at 320°C.

EN measurements have been made for a caustic crevice chemistry under heat flux conditions using the heated crevice. The Alloy 600 tube and simulated TSP in the heated crevice were shorted through a ZRA while the system was operated to produce a caustic crevice chemistry. Figure 8a shows the current noise over a typical 3/4 hour period while the tube was pressurized at 2300 psi. There are numerous positive and negative excursions in the current having amplitudes as large as ± 4 mA. Figure 8b shows the corresponding potential fluctuations of the tube monitored with respect to a Ni rod pseudo reference electrode in the crevice. The potential fluctuations have amplitudes in the tenths of millivolts range. The excursions in potential and current correspond to each other. Figure 8a and 8b shows the current and voltage fluctuations between the tube and simulated TSP when the tube is not pressurized. A comparison of Figures 7 and 8 shows that the current and potential fluctuations from the pressurized tube are three orders of magnitude greater in amplitude that those from the tube which was not pressurized, where the operating parameters of the heated crevice were not changed when the tube was depressurized.



a)

Figure 8 a. Fluctuation in current during SCC in a pressurized Alloy 600 tube in the heated crevice.



b)

Figure 8 b. Fluctuation in potential noise during SCC in a pressurized Alloy 600 tube in the heated crevice.

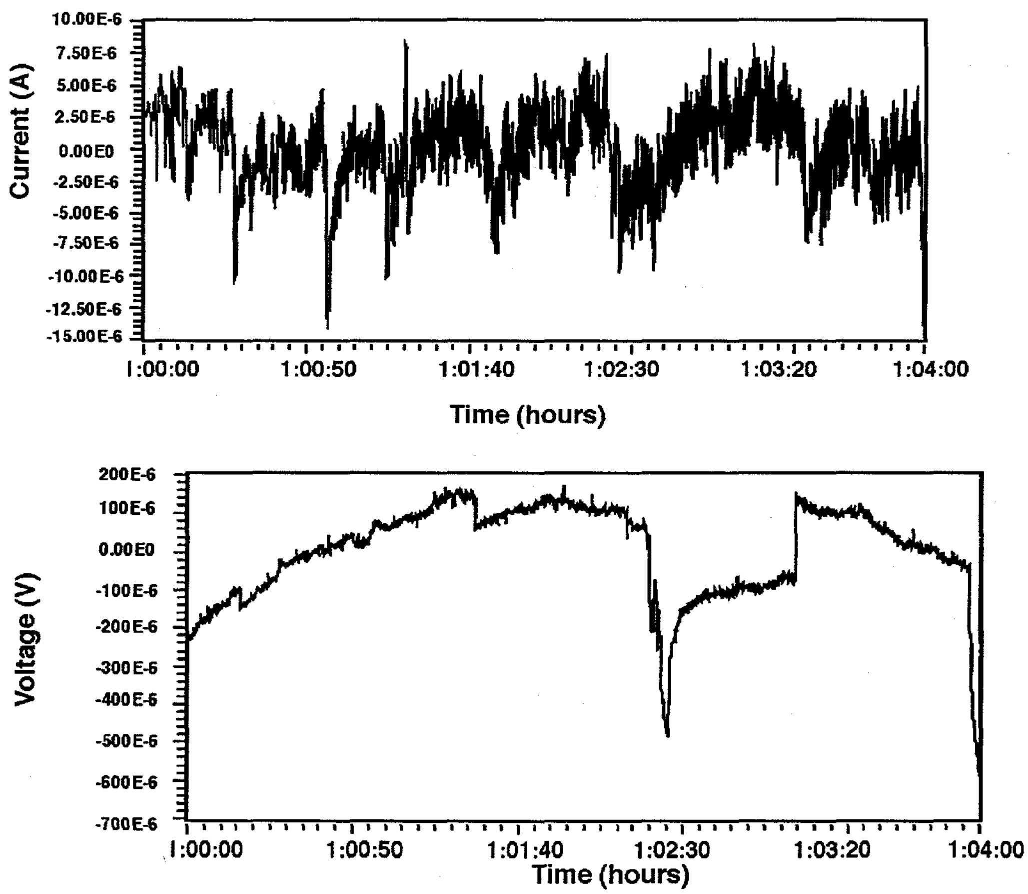


Figure 9. Fluctuation in a) current and b) potential noise in a depressurized Alloy 600 tube in the heated crevice operated to produce a caustic crevice chemistry.

SUMMARY

The objective of Phase 1 of this program was to establish whether EN could be used for *in situ* monitoring of SCC in steam generator tubes in the heated crevice. The work first examined EN from C-ring specimens under conditions shown by several laboratories to produce SCC in Alloy 600. The C-ring specimens were in static autoclaves exposed to 50% NaOH. The current fluctuations were examined over a 48-hour period between a C-ring, which was not loaded and one which had a stress at 150% yield and was polarized at 150 mV above the corrosion potential. There were four 2 to 5 hour periods during which current fluctuations were observed having peak-to-peak values of approximately 8 mA. Between these periods, the peak-to-peak fluctuations were less that 0.5 mA. When the C-rings were removed from the autoclave, a through-wall crack was found in the specimen that had an applied stress. A second autoclave test was run in which current was measured between a C-ring with no stress and one with an applied stress at 150% of yield and polarized at 200 mV. The current was similar to that from the couple at 150% yield and 150 mV except the large current fluctuations ended after 22 hours. The current after 22 hours in the 48-hour exposure period had peak-to-peak fluctuations less than 0.5 mA. Inspection of the C-rings after the autoclave was opened found a through-wall crack in the specimen which had been at 160% yield and at 200 mV. Independent measurements showed that through wall cracks are produced in specimens at 150% yield and 150 mV in approximately 2 days and in specimens at 160% yield and 200 mV in approximately 1 day. These results suggest that the large 0.8 mA peak-to-peak current fluctuations were caused by SCC crack initiation and propagation.

The static autoclave results clearly demonstrated that EN detects SCC of Alloy 600 in a caustic environment. The next step was to evaluate the EN technique during heat flux conditions using the instrumented heated crevice operated to produce a caustic crevice chemistry. The results suggest that EN can be used to monitor SCC in the heated crevice. Pressurizing the Alloy 600 tube caused a pronounced increase in the amplitude of the current fluctuations in the couple formed by shorting the tube to the simulated TSP through the ZRA. Pressurizing the tube while the heated crevice was fully operational also significantly increased the potential noise from the tube measured with respect to a Ni wire pseudo reference electrode.

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