



CORROSION SCIENCE AND ENGINEERING

**ELECTROCHEMICAL NOISE GENERATION DURING CORROSION OF STAINLESS STEEL-TYPE 316
IN ACID CHLORIDE ENVIRONMENT**

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The electrochemical noise generated during the pitting and general corrosion of austenitic stainless steel-Type 316 in acid chloride environment was studied under free corrosion potential and at ambient temperature. The electrochemical noise was observed as spontaneous fluctuation of potential. The observed corrosion behaviours as obtained from the results are related to the existing known pitting/general corrosion mechanism(s) of stainless steels. The clearest indication of results are given by the spectrum standard deviation (essentially the average noise power) the noise voltage density, and the roll-off slope parameters. All the noise amplitudes generally increase with decreasing frequency and the power spectral density is inversely proportional to some power of the frequency, thus indicating '1/f' or 'flicker' noise. The SEM micrograph made from the plastic replicas of the surface of specimens, showed the occurrence of pitting and severe general corrosion.

Key words: Electrochemical noise, corrosion, pitting, spectral density

INTRODUCTION

While noise is a general term used to describe the fluctuating behaviour of a signal with respect to time, the electrochemical noise has been defined as the spontaneous fluctuation of the current passing through an interface (or of the potential) under potentiostatic (or galvanostatic) control [1-3]. For the electrochemical corrosion, the process is stochastic, random in time and is the result of a series of transients associated with film breakdown or local corrosion events. The technique of electrochemical noise measurement is non-perturbative. The analysis of electrochemical noise is known to give useful information about the rate and nature of the chemical processes taking place at the electrodes.

The fact that the amplitude of low frequency potential or current noise (typically at frequencies less than 1Hz) is related to the rate of the corrosion processes and that the shape of the power spectrum is influenced by the nature of the process, has been established. Though little work has been published on this subject in recent years, it is, however, receiving considerable attention [4-8].

In this work, the electrochemical noise generated during the pitting and general corrosion of austenitic stainless steel-Type 316, has been studied under free corrosion potential, in acid chloride solution. The electrochemical noise spectra was correlated with the progress of the (active/passive) corrosion test. In addition, plastic replicas of the corroded surface were made and subsequently examined in the scanning electron microscope.

EXPERIMENTAL

The quantovac spectrographic analysis gave the composition of the austenitic stainless steel as: 0.18C, 0.49Si, 1.39Mn, 0.021S, 0.025P, 8.48Ni, 17.11Cr, 2.0+Mo, 0.03V, 0.17Co, 0.02Ti, 0.021Cu, and the rest Fe. The type 316 austenitic stainless steel, received in seamless tubular form (- 2.13M long) was cut into

C-ring specimens following the procedures previously described [9].

All the specimens were ground with abrasive papers of up to 1200 grit and polished to 1 μ diamond polisher at the portion of the surface subject to maximum tensile stress stretching between the two bolt holes. The solution used for the corrosion test of the austenitic stainless steel specimens was acid chloride-0.5M NaCl/2.5M H₂SO₄ (Analar grade). The solution was poisoned with 200 ppm of sodium sulphide.

The test samples were stressed at a stress of 50% Y.S. (127.2MPa). This was done in part to enhance stress corrosion cracking (if the threshold stress was reached at that stress level) and also to enhance accelerated corrosion of the specimens.

Electrochemical noise measurement

The acid chloride solution was taken into an electrochemical cell and the test specimen was partially immersed in the solution by clamping it to a retort stand. The solution was deaerated for 2 hours with nitrogen gas and the cell was sealed before the noise measurement tests started. A PVC tube was used as a salt bridge to connect the solution to the reference electrode. As previously described [9] the specimen and the standard calomel reference electrode were separately connected to a solartron 7055 digital voltmeter and a chart recorder.

The readings measured by the voltmeter were sent to the computer and stored on a tape. They were then analysed in groups of 1024 in order to construct a frequency spectrum from the time record. (A time record is a record of potential fluctuations over a period of time). Readings were taken every second for about 17.066 minutes (1024 secs.) and a holding time of another 7 hours and 43 minutes giving a total of 8 hours for each time record. The Burg's maximum entropy method was the algorithm used [10].

The spectral density curves obtained for all the data files for each particular specimen were standardised with a uniform scale and then plotted on a single plot. In the spectral density curves (Fig.1) the time (hours) is put in brackets, while the corresponding time records are written by the sides to enhance easy interpretation, better understanding and reading of the curves. Curves of spectral

observed on the surface of the specimens. Further results are based on these later observations.

Electrochemical noise measurement

The selected spectral density curves for the austenitic stainless steel specimens are shown in Fig. 1. The noise amplitudes (voltage density) for the specimens decreased from time record 1 to time record 4 (32 hours from the start of the experiment) and thereafter started to fluctuate up to time record 10 (80 hours from the start of the experiment) with a tendency towards decreasing noise amplitude. This phenomenon continued to time-record 14 (112 hours). A trend of high noise amplitudes at the low frequency of about 1 mHz which decrease with increase in frequency passing 100 mHz was obtained. In Fig. 1 the lowest noise amplitudes were recorded for the specimen at the last seven time records, that is, time-records 14 to 20 corresponding to 112 to 160 hours from the start of the experiment.

Standard deviation (spectrum)/Time curve

The standard deviation (spectrum) vs time curve for the specimen is shown in Fig. 2. There was a decrease of standard deviation

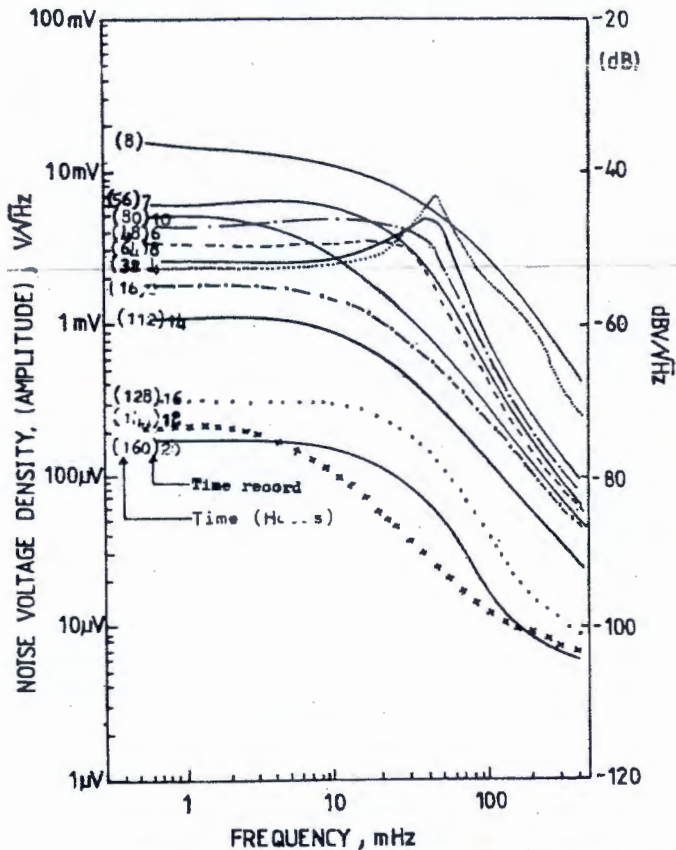


Fig. 1: Selected spectra-austenitic stainless steel (Type-316) in acid chloride environment

density (i.e noise amplitude/frequency) were made. Spectrum standard deviation was the second output obtained from the analysis. These were used to plot the spectrum standard deviation vs time curves. The standard deviation (spectrum) is one of the outputs obtained from the computer analysis of the data from the time domain. It is essentially the average noise power within a spectrum and can be shown to be the area under particular spectral curve in the plot of noise voltage density (amplitude/frequency). Some plastic replicas of the specimens' surface were made before being immersed in the solution and after immersion. The plastic replicas were examined under the scanning electron microscope and micrographs were made.

RESULTS

No failure of the austenitic stainless steel specimens was observed throughout the experimental period of this work, that is, after 16 days of test. However, severe general corrosion and pitting were

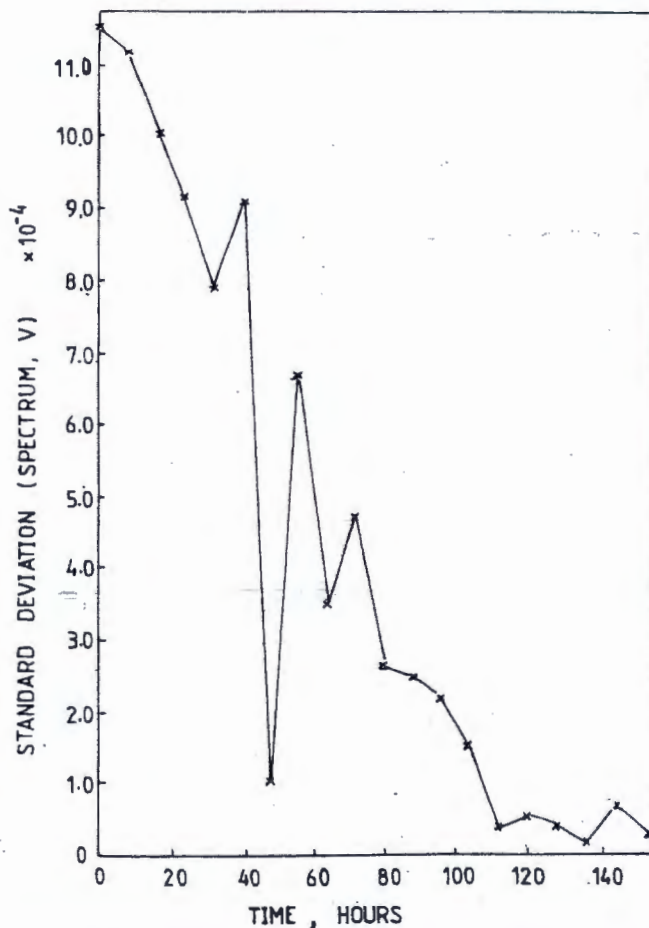


Fig. 2: Standard deviation vs time curve-Austenitic stainless steel (Type 316) in acid chloride environment

with respect to time up to 32 hours from the start of the experiment. Just after this time, a wide fluctuation of standard deviation curve with time could be observed up to the 80th hour from the start of the experiment. A sharp decrease of standard deviation from the 80th to 112th hour from the beginning of the experiment could again be noticed. The last 48 hours of the experiment showed very little variation of standard deviation with time.

Scanning electron micrographs

The scanning electron micrographs made from the plastics replicas of the surface of the specimen are shown in Figs. 3-5. No cracking of the surface of the specimen is discernible. However, severe pitting and general corrosion of the surface of the specimen could be clearly observed.

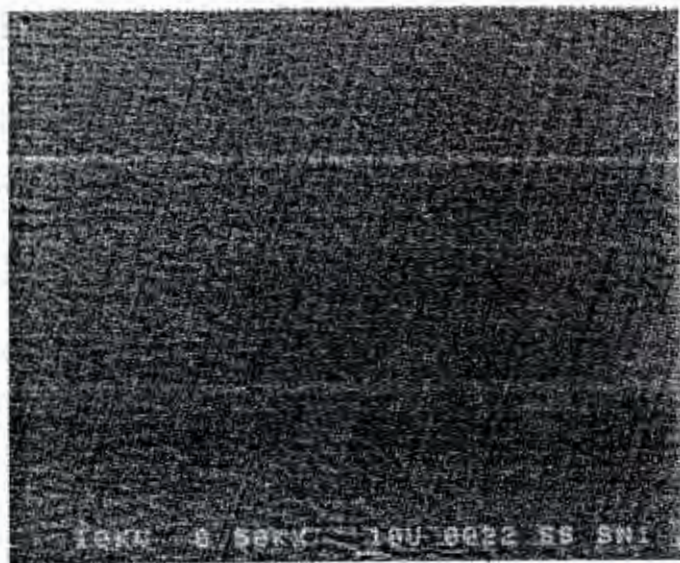


Fig. 3: Plastic replica of the steel specimen's surface before being immersed in acid chloride solution

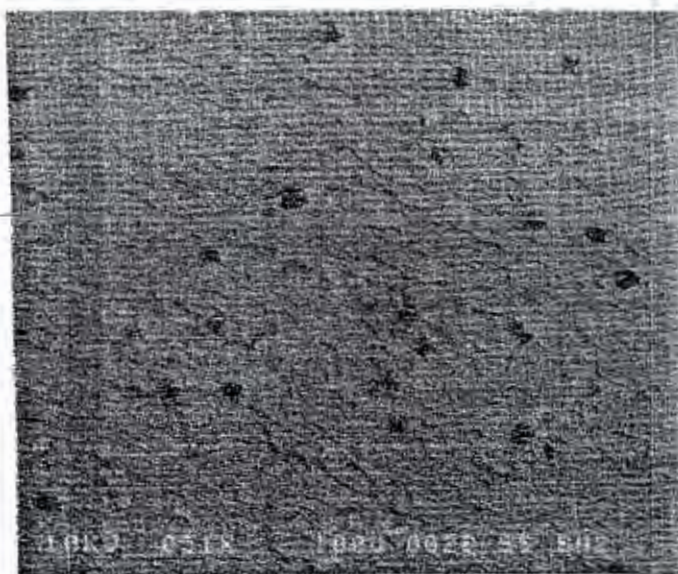


Fig. 4: Corroded surface of the steel specimen in acid chloride solution showing pitting (plastic replica)



Fig. 5: Corroded surface of the steel specimen in acid chloride solution showing general corrosion interspersed with intergranular corrosion as indicated by the channels/grooves on the specimen's surface (plastic replica)

DISCUSSION

Though the test specimens were subjected to a yield stress of 127.2 MPa no cracking was observed in this alloy specimen even after 16 days of experimental work. This might be due to several factors ranging from metallurgical, mechanical, to time factors. The very high molybdenum content (2+ %) of the specimen could also contribute to the stress corrosion cracking (SCC) resistance. It is known that Mo addition to austenitic stainless steels improves resistance to pitting attack by strengthening the passive film and imparting improved corrosion resistance in reducing acids [11-12]. This high Mo content might have accounted for the observed less pitting of the specimen when compared with the general corrosion (Figs.4 and 5). Another reason for the non-cracking of the steel specimens could be due to the stressing method used—the constant strain method and the C-ring form of the specimen in which the

strain might not be enough and the stress not very well concentrated to promote cracking in this type of corrosion resistant alloy. In addition, a yield stress of 127.2 MPa seems to be very low for

the C-ring austenitic stainless steel specimen. It thus indicates that the yield stress of 127.2MPa used was below the threshold stress. It could also be that the experimental period (192 hours) was not long enough at that level to cause a SCC failure.

However, severe general corrosion and pitting, occurred on the specimen's surface. The spectral density curves obtained for the corrosion reaction processes of the specimens are inversely proportional to the frequency, and thus characteristically indicating a low frequency noise, that is, '1/f' or 'flicker noise'. The highest noise amplitude (Fig. 1) occurred at time-record 1 (8 hours) with a roll-off slope of -16dB/decade. This high noise amplitude might be due to the initial diffusion processes of the reacting ions and the effect of film growth. The diffusion fluxes of reaction species at the electrode/bulk solution interface is thought to contribute to the noise generated at the interface [13]. The randomness of the diffusion phenomenon of a corroding metal such as in this investigation, has been explained in terms of the collisions between ions of the diffusing species, and/or ions of the diffusing species with solvent molecules under the influence of the concentration gradient. Diffusion of the reaction species is believed to be involved in the film formation process and it is expected to generate a low frequency noise with its power spectrum inversely proportional to the frequency [14].

The lower noise amplitudes, that is, from time record 2 to time record 4 (16-32 hours) with average roll-off slope of -22dB/decade may be associated with a passive state of the surface of the specimen due to the inhibiting protective film of the stainless steel. The increased (higher) noise amplitude at time record 5 (40 hour) with a roll-off slope of -26dB/decade may be associated not only with film breakdown but also with active corrosion. This is probably the beginning of general corrosion which dominated the whole corroding surface of the specimens. The fluctuations of the spectral density curves (Fig. 1), indicate the random depassivation and repassivation corrosion processes of the surface of the corroding specimens in the test medium. The noise amplitudes at the low frequency, in particular, were very random and this could be due to the potential fluctuations of the corrosion reactions.

The last seven time-records, that is, time-records 14 to 20 (from 112 to 160 hours from the start of the experiment), gave the lowest noise amplitudes. A drastic reduction of corrosion reactions caused apparently by the stifling effect of the observed heavy precipitation of the corrosion products on the test electrodes in the corrosion cell, must have necessitated this phenomenal corrosion behaviour. These recorded lowest noise amplitudes could also be due to the intense contamination of the test solution by the corrosion products, lessening its chemical reactivities.

In this specimen, generally, a roll-off slope of -20 to -21 dB/decade could be associated with general corrosion and anodic dissolution phenomena. These cover mostly the periods ranging from time-records 6 to 14 (48 to 112 hours).

The aggressiveness of the test solution—the poisoned acid chloride used, could have considerable impact on the rupturing of the passivating film due to the penetration of the chloride ions, Cl-

and sulphide ions, S²⁻. The rate of film breakdown could be more than the repassivation process. The tendency then would be that more of the fresh bare metal surface, which was more active than the rest of the metal surface, was exposed to the solution. This fresh surface, before becoming inhibited itself by the growth of a new film, dissolved preferentially by anodic dissolution process and thus causing pitting and general corrosion of the test electrodes. The rupturing of the passivating film might be expected to have been further enhanced by the effect of the applied stress on the specimens, which is due to the inhibiting film covering the metal surface that could be partially ruptured by emergent dislocations activated by the applied stress. This rupture, in addition to the penetration of Cl⁻ and S²⁻ ions into the film (earlier mentioned), caused a fresh metal surface to be exposed to the corrosive medium with a consequential effect of surface corrosion.

The noise generated from general corrosion might be as a result of inhomogeneous surface created by the anodic and cathodic reaction processes. The same explanation could also be used to explain the noise generated from pitting of the specimen in the test environment. Since, surface inhomogeneity has been a major cause of noise generation for pitting and general corrosion (in addition to the noise generated by the reacting ions), it then becomes difficult to characterise these two corrosion forms differently by the roll-off slopes. Similar results such as mentioned above have also been reported by other investigators [4,6,14-17]. The reactions occurring during the general corrosion and pitting of the surface of the specimens are random processes [3]. These result into random fluctuations thereby giving rise to noise.

The standard deviation (spectrum)/time curve, Fig. 2, corresponds with the spectral density curves. The correspondence is expected since the spectrum standard deviation is the average noise power within a spectrum and can be shown to be the area under a particular spectral curve.

SEM micrographs made at the end of the test also show pitting and general corrosion processes (Figs. 4 and 5). Mechanistically, the observed corrosion processes as obtained from the spectral density curves, standard deviation (spectrum) vs time curves and the SEM micrographs, seem to be consistent with film rupture/anodic dissolution mechanism.

CONCLUSION

Austenitic stainless steel-Type 316 can undergo severe general corrosion and pitting in acid chloride environment at ambient temperature. The electrochemical noise measurement technique can be used to monitor the corrosion processes of the alloys under free corrosion potential. A low frequency noise with '1/f' or 'flicker' noise is indicative of the corrosion processes. The source of the electrochemical noise is believed to be from the diffusion of the reacting species and the active/passive corrosion processes that is the depassivation (film rupture) and repassivation transients of the specimen's reacting surface and the inhomogeneous specimen surface resulting from pitting general corrosion.

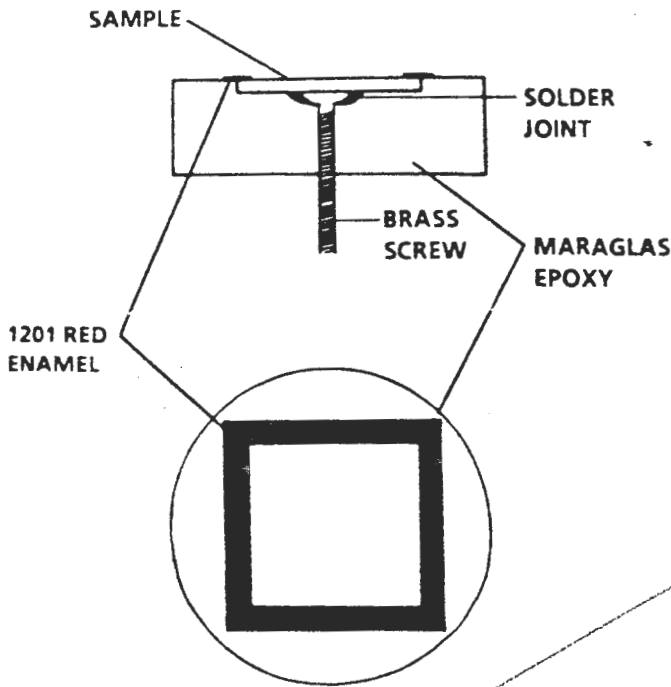


FIGURE 1. Schematic representation of a corrosion sample with the metal/epoxy mount interface coated with protective enamel.

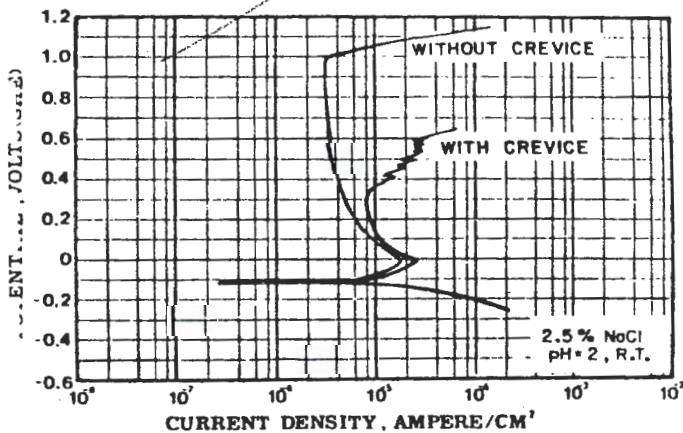


FIGURE 2. Polarization curve for AISI 316L SS (a) without and (b) with crevice corrosion (2.5% NaCl at 27 C, pH = 2, 3 V/h).

cal) compositions within an alloy class. By a large margin, the major compositional variable in the set of alloys depicted in Figure 4 is the nitrogen content, which varied from 0.02 to 0.17% with essentially constant Cr (20.5%), Mo (0.2%), and C (0.05%). As is obvious from the data in Figure 4, no significant effect of nitrogen would have been observed without the prepassivation treatment. For the test condition including the prepassivation treatment, the post-test surface generally revealed several pits far removed from the metal/enamel interface with no other indication of attack.

The above observations led to a re-examination of the mechanism of crevice corrosion, particularly how it is initiated. During a potentiodynamic upscan starting at the corrosion potential in the active region, metal dissolution occurs with a relatively high corrosion rate on the entire surface until the passive film forms. The metal ions dissolved from the bulk surface spread out into the bulk solution. However, inside a crevice at the metal/enamel interface or the metal/epoxy interface, an accumulation of metal ions occurs

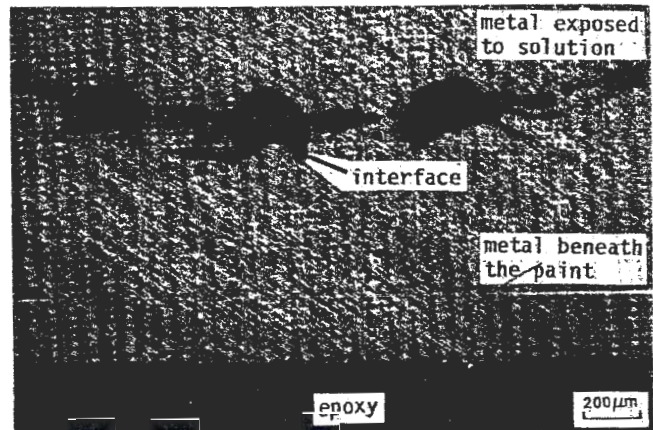


FIGURE 3. Representative appearance of crevice corrosion at the interface between the metal and the enamel for a non-prepassivated sample.

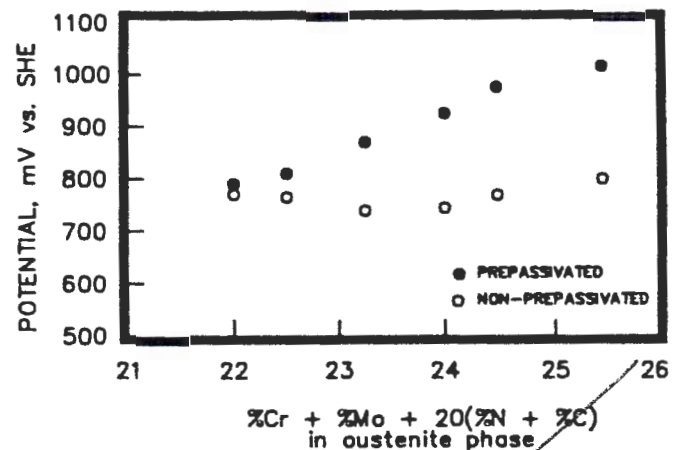
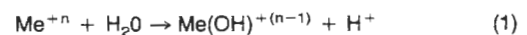


FIGURE 4. Comparison of the pitting potential determined for prepassivated surface by standard cyclic polarization and that determined for surface without prepassivation for solution-treated CF-8 alloys. All other procedure variables remain constant (1 N sulfuric acid with 0.5 M NaCl at 27 C, 3 V/h).

because of the restricted fluid condition, resulting in an increase in acidity by the reaction,



Crevice corrosion occurs when the potential during upscan and the increasing acidity reaches values that cause breakdown of the passive film.⁷ However, if the sample is prepassivated before application of the enamel, the metal dissolution rate inside a possible crevice is very low and the above reaction is restricted. Therefore, the conditions favorable for crevice corrosion are reduced for prepassivated samples.

Since crevice corrosion occurs at much lower potentials than the pitting corrosion in a given alloy/environment combination, the conclusion is that many reports of pitting potentials in the literature are actually potentials for crevice corrosion at the interface between the specimen and the mounting material.

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Electrochemical Noise Generation During Stress Corrosion Cracking of the High-Strength Aluminum AA 7075-T6 Alloy[☆]

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ABSTRACT

Electrochemical noise generation during stress corrosion cracking (SCC) of high-strength aluminum AA⁽¹⁾ 7075-T6 alloy has been investigated in 3.5% NaCl solution under free corrosion potential. The electrochemical noise was observed as spontaneous potential fluctuations. The readings obtained were analyzed using the maximum entropy method. In the results, the power spectra densities were found to decrease with an increase in frequency. A low frequency (LF) noise was obtained with all the specimens tested and it characteristically indicated LF or "flicker" noise. The noise generated from the corroding specimen/bulk solution interface was found, generally, to increase with the degree of corrosion. The cracking of the specimen gave the highest noise amplitudes in most cases; the cracking is also indicated by the highest standard deviation peaks. The results obtained for this aluminum alloy further show the corrosion cracking behavior to be consistent with the film rupture/anodic dissolution mechanism.

INTRODUCTION

The phenomenon of electrochemical noise generation during corrosion and other electrochemical processes has received considerable attention¹⁻⁹ in recent years. It has been found that the amplitude of the low frequency (LF) potential or current noise (typically at frequencies <1 Hz) is related to the rate of the corrosion processes and that the shape of the power spectrum is influenced by the nature of the process. While it has been suggested that stress corrosion cracking (SCC) might be expected to give a characteristic noise spectrum (particularly if the cracking is occurring by a process of film rupture/anodic dissolution), little systematic work has been published on this subject. In the current work, the electrochemical noise generated during the SCC of the high-strength aluminum alloy AA 7075-T6 in 3.5% NaCl solution has been studied, and the electrochemical noise spectra correlated with the

progress of the stress corrosion test. In addition, various experiments have been performed in which the progress of the crack initiation and growth has been followed using plastic replicas taken from the surface and subsequently examined in the scanning electron microscope (SEM). Attempts are made in this work to relate the observed corrosion behaviors, as obtained from the results, to the existing known SCC mechanisms.

The results obtained in this work were analyzed using Burg's maximum entropy method (MEM).¹⁰ The method mathematically ensures that the fewest possible assumptions are made about unmeasured data by choosing the spectrum that is the most random or has the maximum entropy for the process under investigation and is consistent with known data.¹¹ The maximum entropy method of spectrum analysis considerably improves the spectral resolution for short records over what can be obtained with conventional techniques.¹² This is achieved by extrapolation of the auto-correlation function so that the entropy of the corresponding probability density function is maximized in each step of the extrapolation. The method makes no assumption of the data outside the time interval specified and, thus, is least committing to the unavailable data. Burg's method is data dependent and, therefore, in this sense, is nonlinear. The method has been described¹³ to enhance the peaky component of the spectrum. It has the advantage of giving smooth spectra, although its applicability to large record sizes, such as used in this work, may be questioned. However, it is not expected that an alternative analysis, such as the Fourier transform, would give significantly different results in respect of the main parameters used in the interpretation of the results.

The LF noise (also called flicker noise) with the LF noise characteristics obtained, as mentioned in the abstract and in the discussion, is not completely understood. It has been seemingly described to be associated with the conduction processes in granular semiconductor material or with cathode emission which is governed by diffusion of clusters of barium atoms to the cathode surface when first observed in vacuum tubes. This noise was called the flicker effect, probably because of the flickering observed in the plate current.¹⁴ LF noise has several unique properties. The spectral density of this noise increases without limit as frequency decreases. It generally dominates thermal or shot noise at frequencies <100 Hz. In many cases, its power spectrum is inversely proportional to the frequency.

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EXPERIMENTAL PROCEDURE

The aluminum alloy, AA 7075-T6, used in this study was specially heat treated to render it more susceptible to SCC. It contained 93.2% Al, 2.1% Mg, and 4.7% Zn. The test specimens obtained as tubular extensions were cut 15-cm long, 4.45 cm in outer diameter (OD), and 0.65-cm thick (t). The tubes were cut into C-ring specimens (Figure 1). That portion of the surface exposed to the maximum acting tensile stress was ground to 1200 grit using abrasive papers and then polished to 1 μ -polisher. The Analar grade NaCl was used to prepare 3.5% NaCl solution using distilled water. The specimens were stressed by tightening a bolt and nut to reduce the ring diameter of each of the specimens. A micrometer was used to measure the OD of the specimen parallel to the stressing screw; the wall thickness was also measured. The desired stress, in terms of the properties and dimensions of the specimen, was determined using the following equations:¹⁵

$$\text{OD}_f = \text{OD} - \Delta \quad (1)$$

$$\Delta = f\pi D^2/4Etz \quad (2)$$

where: Δ = change of OD, giving desired stress (mm); f = desired stress (MN/m^2); OD = outside diameter before stressing (mm); t = wall thickness (mm); D = mean diameter (OD - t)mm; E = modulus of elasticity (MN/m^2); Z = a correction factor or a constant function of ring D/t (Figure 2); and OD_f = final OD of stressed C-ring (mm).

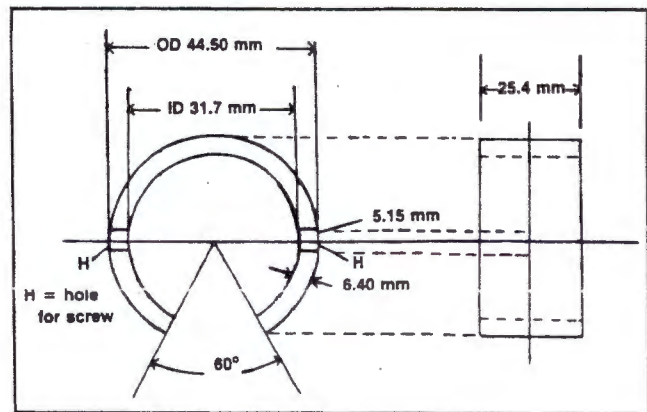
Preliminary tests of time-to-fracture at various percentages (%) of yield stress levels were conducted. These were done to give an idea of the cracking time of the alloy specimens.

Electrochemical Noise Measurement

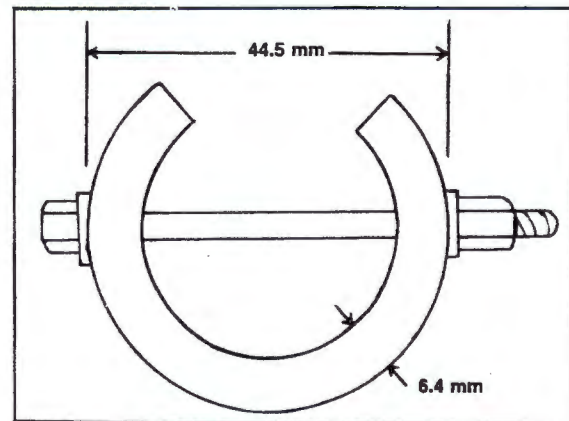
The electrochemical noise measurement for the SCC testing was conducted using a beaker (500 cc), half-filled with 3.5% NaCl solution. The C-ring aluminum alloy specimen, stressed at 75% of yield stress (429 MPa), was partially immersed into the solution. It was hung with a clamp, which was also clamped to the retort stand.

The aluminum alloy specimen and the reference electrode (SCE) were connected respectively to a Solartron[†] 7055 digital voltmeter which measured the potentials. The digital voltmeter was connected to a Hewlett-Packard⁽²⁾ HP85 desktop computer which controlled the voltmeter. The readings measured by the voltmeter and taken every second for ~17.066 min. (1024 s) were sent to the computer where they were stored on tape. Some minutes were allowed as the holding time before the next reading began. The readings were then analyzed in groups of 1024 using a Hewlett-Packard HP85 desktop computer to construct a frequency spectrum from the time record using an algorithm based on the maximum entropy method.¹⁰ A time record is a record of potential fluctuation over a period of time.

The spectra density curves obtained for all the data files for each particular specimen were standardized into a uniform scale and then plotted on a single plot or more, depending upon the number of data files for a specimen. All the curves were for spectral density [i.e., noise voltage density (amplitude) vs frequency]. A spectrum which characterizes the frequency content of a random signal is the power density spectrum or spectral density. The spectral density describes the power of the frequency components of the signal but not their phases. The second output obtained from the analysis was that of spectrum standard deviation for each data file. The standard deviation (spectrum) is one of the outputs obtained from the computer analysis of the data from the time domain. Essentially, it is the average noise power within a spectrum and can be shown to be the area under a particular spectral curve



a



b

FIGURE 1. (a) Al alloy C-ring specimen preparation for stress corrosion test; (b) Al alloy C-ring specimen.

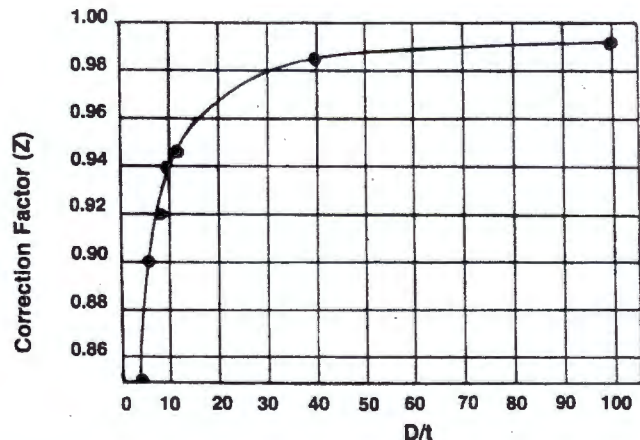


FIGURE 2. Z correction factor used in formula by which C-ring stress is calculated.⁹ (After Craig, et al.)

in the plot of noise voltage density (amplitude)/frequency. The standard deviation of random variable measures the orders of magnitude of the fluctuations about the mean at any chosen point of time. These were extracted and used to plot the spectrum standard deviation vs time curves. The representation of a time-varying process in the frequency domain is called a spectrum.

Experiments were conducted similarly and readings analyzed for various unstressed specimens as for the stressed ones. Vari-

[†]Registered trademark.

⁽²⁾Hewlett-Packard Computer Products/Digital Resources, Inc., Portland, Oregon.

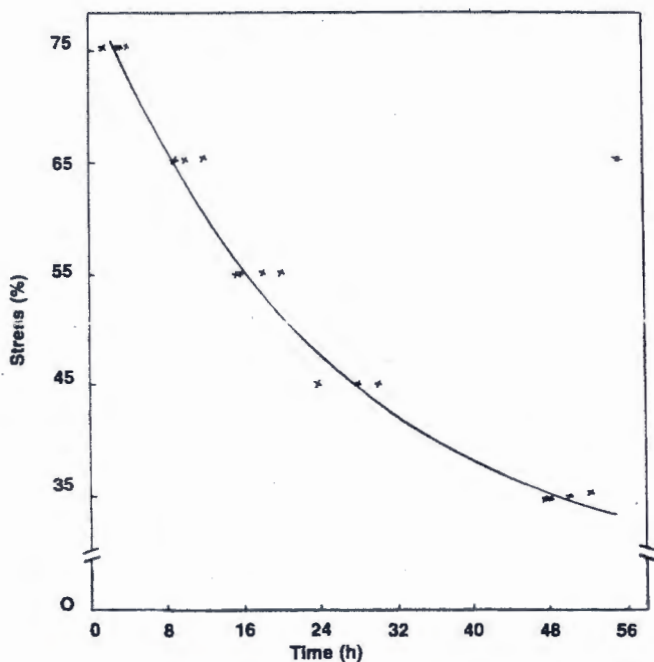


FIGURE 3. Time-to-failure vs applied stress — Al alloy.

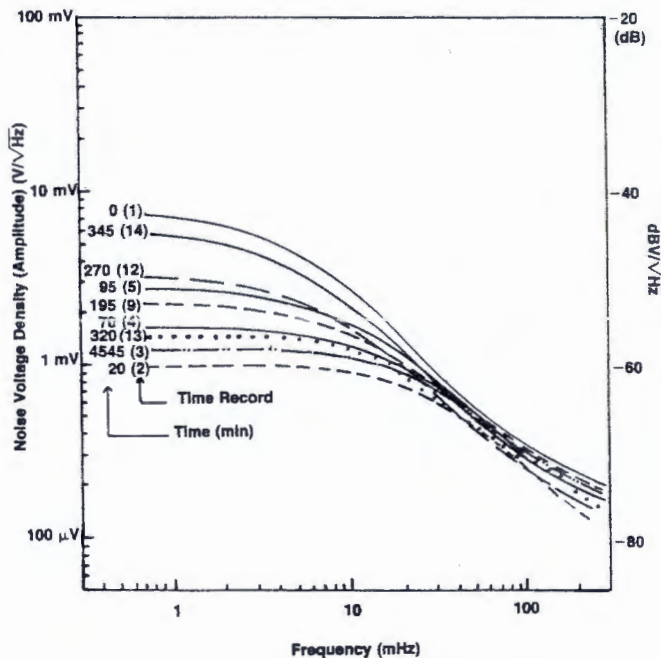


FIGURE 4. Selected spectra — Al alloy, no stress.

ous experiments were also performed in which the progress of the crack initiation and growth was followed using plastic replicas taken from the surface and subsequently examined in the SEM.

EXPERIMENTAL RESULTS

Stress and Time-to-Failure

The curve of time-to-failure (Figure 3) shows that the failure time increases with a decrease in the percentage of stress and *vice versa*. While the time-to-failure at 75% yield stress (429 MPa) was ~2 1/2 h, it took 4 h for the specimen stressed at 35% of yield stress (200 MPa) to fail.

Electrochemical Noise Measurements — Spectral Density Curves

Figures 4 and 5 show the curves of the noise voltage density (amplitude) vs frequency (the spectral density curves). No failure was observed in the unstressed specimen (Figure 4). In the spectral density curves (Figure 4), the highest noise voltage density is shown at Time Record 1 and the lowest noise amplitude is shown at Time Record 2 (20 min.). The spectral curves become very close together after the frequency of 10 mHz. Although the curves of Figures 4 and 5 look similar in shape, sharing a LF noise characteristics and with almost similar corrosion reaction processes in the first 120 min. of the experiment, discernible features occurred after the 150th min. (Time Record 7). This is made clearer in the corresponding Figure 6.

In the stressed specimens, as exemplified in Figure 5, the times of crack initiation and failure are, in most cases, those that correspond with the highest noise amplitude at the LF levels (0.1 to 1.0 mHz.). The same trend can also be observed at the higher frequencies of 10 and 100 mHz. For example, the highest noise amplitude occurred at Time Record 10 (220 min. from the start of the experiment). This was observed to be the time that the crack first became discernible. In the spectral density curves (Figures 4 and 5), the time record figures are put in brackets, while the corresponding time (min.) are written beside them.

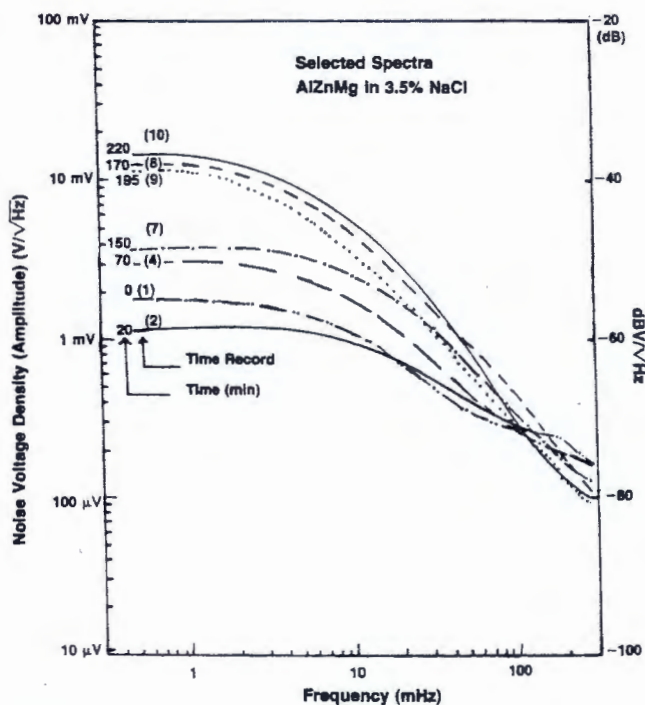


FIGURE 5. Selected spectra — Al alloy, stress of 429 MPa.

Standard Deviation (Spectrum) vs Time Curves

The unstressed specimen gives a standard deviation curve (Figure 6), which varies randomly with time. The first time record gives the highest peak. A zig-zag form of curve is shown after Time Record 6 (120 min.). A sharp fall of standard deviation occurs at Time Record 2 and thereafter rises with time to Time Record 5. In all of the observed stressed specimen curves, the highest peaks denote the failure time. In Figure 6, for example, the

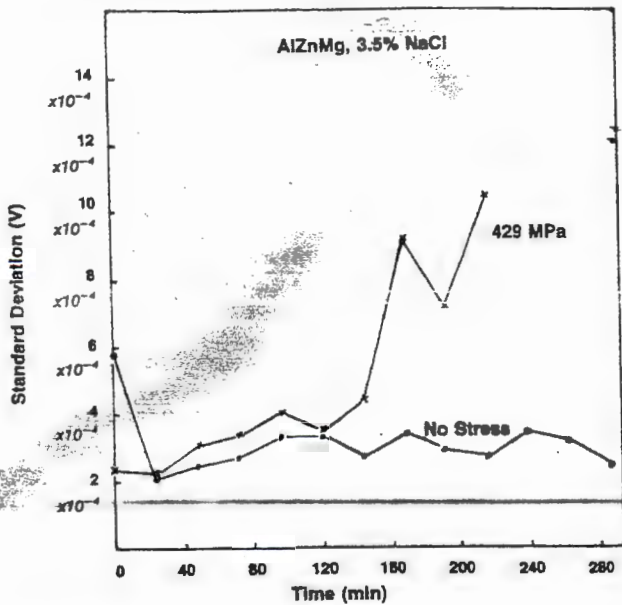


FIGURE 6. Standard deviation vs time — Al alloys, stresses of 429 MPa and unstressed.

highest peak for specimens stressed at 75% of the yield stress (429 MPa) corresponds with a time of 3 h 36 min. The standard deviation (spectrum) vs time curves (Figure 6) gives results that can be correlated with the spectral density curves. The cracking time which is indicated by the highest standard deviation peaks are observed to correspond with the highest noise amplitude in the spectral density curves.

SEM MICROGRAPHS

The SEM micrographs made from the stressed specimens are the negative image of the actual surface (Figures 7 and 8); hence, pits are shown as "bumps" and cracks appeared as "ridges." Pits could be seen to have developed within the first 30 min. in solution. As at 40 min. (Time Record 3), the microcracks could be observed to have initiated from pits (Figure 7). This occurrence could be correlated with the high-noise amplitude and the high standard deviation peak observed in Time Record 3. At ~3 1/2 h, crystal grains could be seen from the point of cracks and within the pits (Figure 8). This occurrence and the time corresponds with Time Record 9 (195 min.) on the spectral density curve (Figure 5).

Cracking in this alloy specimen (Figure 9) could be observed to have passed through the grain boundaries and, thus, show intergranular failure which is characteristic of SCC.

DISCUSSION

The major mechanism of cracking proposed by various authors¹⁷⁻²¹ for the SCC of high-strength aluminum alloys is the film rupture/anodic dissolution mechanism, although the hydrogen embrittlement mechanism has also been proposed by various workers. Attempts are being made here to relate the results obtained in this work with the above presented mechanisms.

The general trend of corrosion behavior of corroding test specimens (stressed and unstressed) is that at the beginning, there was a fairly high noise amplitude as indicated, for example, by the spectral density and the peaks of the standard deviation curves. This may be associated with the initial growing in the solution of the air-formed passive film oxide or hydroxide, which might have caused some potential transients resulting from the chemical



FIGURE 7. Al alloy specimen surface after 30 min. in solution. (Negative image from plastic replica.)

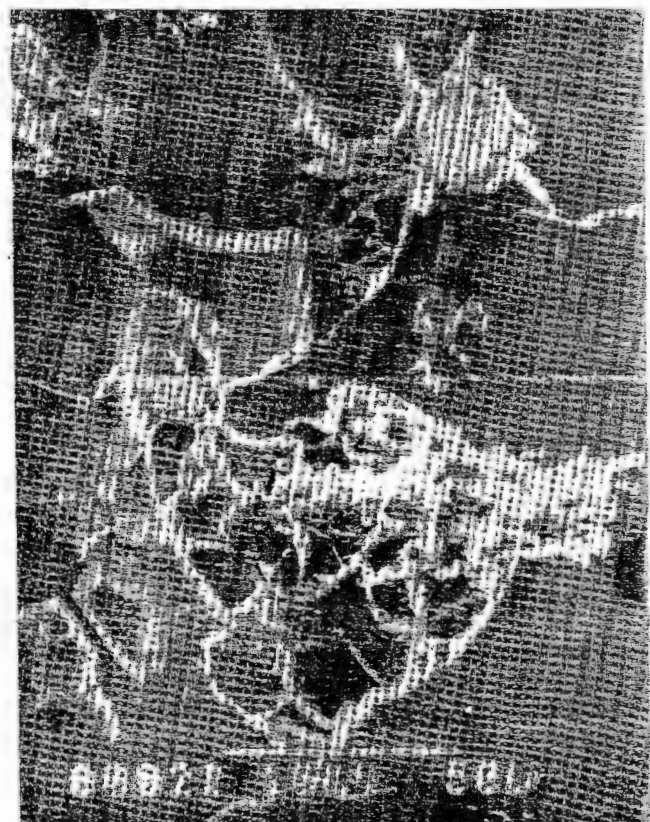


FIGURE 8. Grain crystals within pit formation and the cracked surface of the Al alloy specimen after 60 min. in solution (negative image).



FIGURE 9. Fractured surface of the Al alloy specimen (showing intergranular failure).

reactivity and the ion diffusions associated with the passive film oxide formation. The high-noise amplitude was followed by an immediate fall or decrease of noise, which may be associated with passivity. There was a further random increase of electrochemical noise, which may be associated with pitting, particularly with the stressed specimens. The highest noise amplitude was obtained at the time that the crack first became discernible in the stressed specimens.

All the spectral curves of the unstressed alloy are inversely proportional to the frequency or to some power of frequency. The noise amplitudes are distinctly separated from each other for different times at the LF ranges (0.5 to 10 mHz). The above observations indicate a LF noise, and they appear to conform with the characteristics of LF or "flicker" noise. The highest noise amplitude at Time Record 1 (0 to 20 min.) (Figure 4), with a roll-off slope of -17 decibel (db)/decade may be associated with the initial growth of the passive film on the specimen's surface, as explained above. The lowest noise amplitude at Time Record 2 with a roll-off slope of -11 db/decade could be associated with the subsequent passivity. The increase in the noise amplitude as shown by Time Record 3 (45 min.) to Time Record 5 (95 min. from the start of the experiment) with an average roll-off slope of -12 db/decade seems to indicate film breakdown process and probably the onset of pitting. While the low-noise amplitude of Time Record 13 probably shows a repassivation process, the higher noise amplitudes of Time Records 12, 14, and 15, with roll-off slopes of -15 , -17 , and -16 db/decade, respectively, may be associated with increased pitting. The standard deviation (spectrum)/time curve (Figure 6), with its alternating peaks, could also be used to interpret the film breakdown and repair phenomenon of the corroding process.

The corrosion processes of film breakdown, film repair, and pitting, as observed in this work, might have been the source for the increase and decrease in noise amplitudes. The potential fluctuations resulting from the dynamic equilibrium process may be explained by the random breakdown and repassivation transients occurring from the corroding process. The amplitude and the frequency of the potential fluctuations may depend on the degree of

the uniformity of the film and the time necessary for repairing breaks.

The stressed specimens, as indicated in the curves of Figures 5 and 6, show initial similar characteristics as the unstressed specimens with respect to the corrosion processes described above. The major different corrosion reaction characteristics could be observed only during the crack initiation and propagation periods (Figure 6).

The noise amplitude for Time Record 1 is low with a roll-off slope of -11 db/decade, unlike the higher noise amplitude and roll-off slope for the Time Record 1 in the unstressed specimen. Like the unstressed specimen, Time Record 2 here has the lowest noise amplitude with a roll-off slope of -9 db/decade. The lowest noise amplitude of the Time Record 2 could result from the passivity of the specimen's surface. With passivity, the chemical reactivities and the diffusion fluxes of reaction species will be minimal; hence, the potential transients will be low, as shown by the lowest noise amplitudes.

From the roll-off slope associated with this phenomenon here and that of the unstressed specimen, as given above, lower roll-off slope of -9 and -10 db/decade could, therefore, be associated with passive state of the surface. The increase in noise amplitude from Time Records 3 through 7 (150 min. from the start of the experiment) with a consistent roll-off slope of -13 db/decade could be associated with the initiation of cracking and/or pitting of the specimen's surface. A drop in noise amplitude at Time Record 6 with a roll-off slope of -10 db/decade may, however, suggest a repassivation process.

Time Records 8 through 10 have the highest noise amplitude, and they are higher than any of the time records in the unstressed specimen's spectral density curves. This could be an indication of crack growth. The chemical reactivity with fresh bared metal surface created by the crack growth and which results into active dissolution of the electrode surface might have contributed to the increased potential transients during this period and, hence, the highest noise amplitude recorded. The roll-off slope for Time Records 8 and 9 are -17 and -20 db/decade, respectively, while for Time Record 10 (220 min.), it is -22 db/decade. The period from Time Record 8 to 10 could be associated with the crack formation and growth, although Time Record 10 is where the specimen's crack first became discernible. A roll-off slope of -20 and -22 db/decade could then be associated with pitting and crack growth.

The results obtained for the roll-off slopes, as discussed here, are in a range which appears to be in agreement with previous works.^{1,3-9,16} No significant difference occurred in noise amplitude for most of the experimental period (up to Time Record 7) and the roll-off slopes between the unstressed specimen and the stressed specimen, as exemplified in Figure 5. This may indicate that similar corroding processes of nearly the same degree/magnitude occurred in both specimens during these periods. There was evidence of hydrogen generation with the formation of bubbles around this time, which may suggest a probable hydrogen embrittlement process. Generally, roll-off slopes show a tendency of becoming increasingly negative with the increase in the degree of corrosion.

The standard deviation/time curves are very much related to the spectral density curves, and their variations with time correspond exactly with the spectral density curves, as indicated by the time record numbers (Figure 6). The initial high standard deviation can probably be related to the growing film on the specimen's surface and the subsequent anodic corrosion processes involving film breakdown after passivity. The immediate fall of the standard deviation curve could be associated with the film repair and the subsequent rise of the curve, with film breakdown and the onset of pitting. A further rise of the standard deviation curve with time, for example in Figure 6, may be associated with further pitting and the deepening of pits. The highest standard deviation peak is that where the cracking occurred.