

THE MEASUREMENT OF LOCALIZED CORROSION USING ELECTROCHEMICAL NOISE*

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Abstract - Measurements of self-generated electrochemical potential fluctuations on electrodes undergoing either pitting or crevice corrosion show that these forms of localized attack have quite distinct noise "signatures" and that these two types of attack can be detected within seconds of their initiation.

INTRODUCTION

SEVERAL workers have investigated electrochemical noise related to electrode processes. Barker¹ concluded that noise measurements should be productive when applied to systems where charge transfer is catalyzed by a minor component of the interface or where the system is remote from its equilibrium. Blanc *et al.*² investigated the iron/sulphuric acid system using a cross-correlation technique. Hagyard, Earl and Prior³ observed free corrosion potential variations on aluminium electrodes and ascribed these to the formation of microanodes within oxide film cracks.

In the present work the potential changes occurring on naturally corroding electrodes were observed using two platinum reference electrodes and a two channel high gain amplifier system.

The cell configuration and reference electrodes were designed to present a low impedance source to the detection circuitry. The test cell used a "Quickfit Visible Flow" 3-1 in. reducer piece as the cell body with a 45 cm² test electrode bolted to the lower 3 in. end by standard "QVF" sleeve and gaskets. After filling with 300 ml of test solution the two platinum reference electrodes were inserted through the upper opening. The reference electrodes were *ca* 5 cm lengths of thin platinum wire, sealed in glass tubing with connections via low noise miniature screened cable. The platinum wire was coiled round the outside of the glass tubing in order to minimize effects of vibration.

Although this type of electrode lacks a well defined half cell potential, compared to standard calomel reference electrode, its low impedance makes it ideally suited to the present purpose. The authors' opinion is that calomel reference electrodes are unsuitable for low level signal measurements because of their extreme susceptibility to electromagnetic and acoustic pick-up.

The major obstacle encountered in this type of measurement is that the required noise signal, measured in microvolts, is superimposed on a d.c. level of several hundred millivolts. For the present purpose a system of amplifiers was built using readily available components, following the general outline of a circuit published elsewhere⁵, with a low frequency cut off point of 0.1 Hz and overall gain of 80 dB

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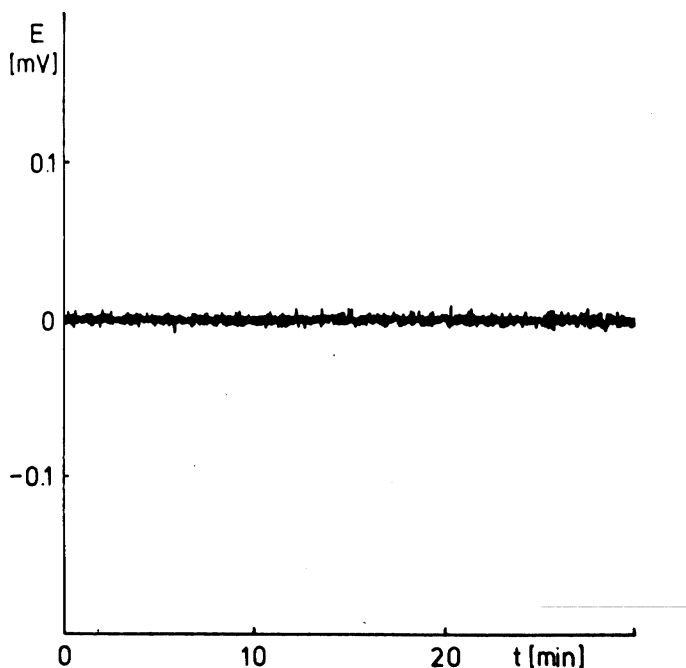


FIG. 1. Electrode noise output prior to chloride ion addition.

(10,000 times). Standard commercial operational amplifiers of the "355" type were used throughout, resulting in a circuit noise level referred to the input of less than 0.1 microvolt rms above 1 Hz, rising to 1 microvolt rms at 0.008 Hz.

Two identical amplification channels were constructed, one for each of the reference electrodes. In practice the two channels "tracked" extremely well, the same electrode noise signal appearing at the two amplifier outputs.

External pick-up levels and cross-talk between the two channels were found to be below the noise level of the amplifiers used.

EXPERIMENTAL METHOD

The test electrodes were abraded to "200" grit size, rinsed with distilled water and assembled in the test cell. During the experimental runs the amplifier outputs were monitored on a storage oscilloscope (Telequipment DM64) and via a pair of high impedance stereo headphones (Sennheiser HD414). One channel was recorded continuously on a chart recorder (Servoscribe 1s); a second chart recorder was used to monitor the d.c. (0-0.1 Hz) component of the reference electrode signal available at the first stage of the amplifier circuit.

The first experimental system used mild steel in 1000 ppm sodium chloride solution inhibited by a 1000 ppm concentration of sodium nitrite. This has been investigated previously in some detail by several workers, including the present authors,⁴ and was found to result in pitting or crevice attack. The second system reported here also used mild steel but with 1000 ppm of potassium dichromate and 1000 ppm sodium chloride. In both cases the electrodes were first immersed in solutions free of sodium chloride and only after a period of 5-10 days was the chloride added.

RESULTS

Prior to the sodium chloride additions both of the systems tested exhibited noise output levels below those of the amplifiers (Fig. 1).

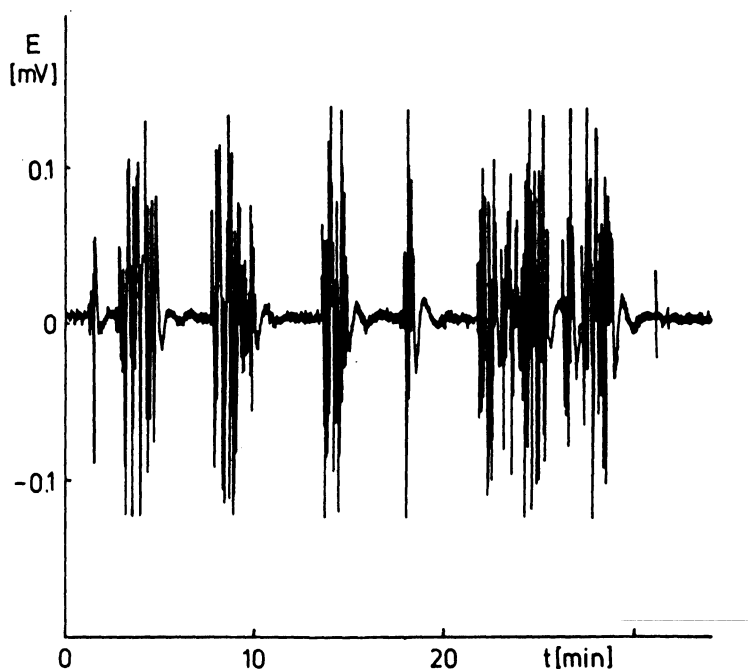


FIG. 2. Electrode noise output during pit initiation period.

1000 ppm NaNO₂ + 1000 ppm NaCl

Approximately 30 s after chloride ion addition, the first burst of noise was observed (Fig. 2) followed by similar noise bursts every 10-15 minutes during the next 10 min of this particular run. A small pit was visually detected on the electrode after seven days. The d.c. potential of the electrode, previously nearly constant, began to vary after the chloride addition, exhibiting a distinct cyclic behaviour (Fig. 3). Starting from an anodic value the potential dropped linearly with time, typically 2(1-50 mV, in less than 1 min, suggesting a process exhibiting a constant current behaviour. This part of the cycle also corresponded to the high noise output--a noise burst. During the next part of the cycle the potential rose exponentially towards its original value, the "time constant" of the process being in the order of 1400 s. The cycle then repeated with the repassivation (exponential) portion sometimes interrupted by a second potential drop.

In order to investigate the effects of chloride ion concentration the chloride level was increased to 2000 ppm after five days of measurements and the observed time constant decreased to some 900 s. After a further five days the chloride concentration was increased to 4000 ppm and a similar decrease in the time constant was observed. Before any further measurements could be made the electrode began to exhibit crevice corrosion.

The change from pitting to crevice attack was first observed as a change in the pattern of the electrode potential behaviour. The cyclic movement of the d.c. potential was replaced by a general random drift interspersed with short periods of the cyclic

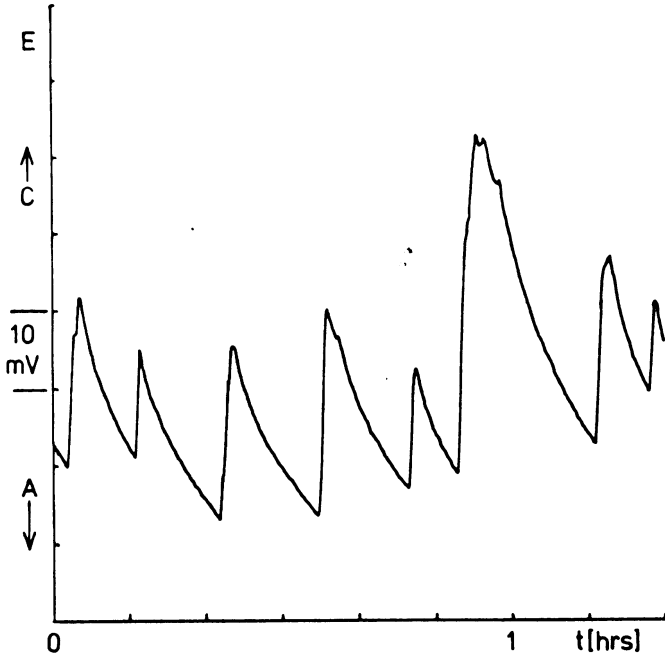


FIG. 3. D.C. component during pit initiation period.

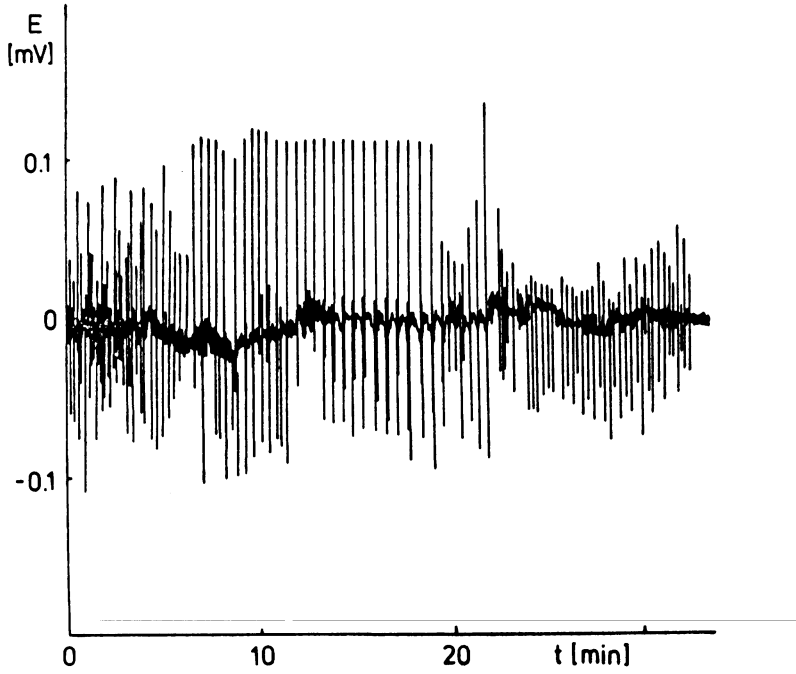


FIG. 4. Electrode noise output during crevice attack.

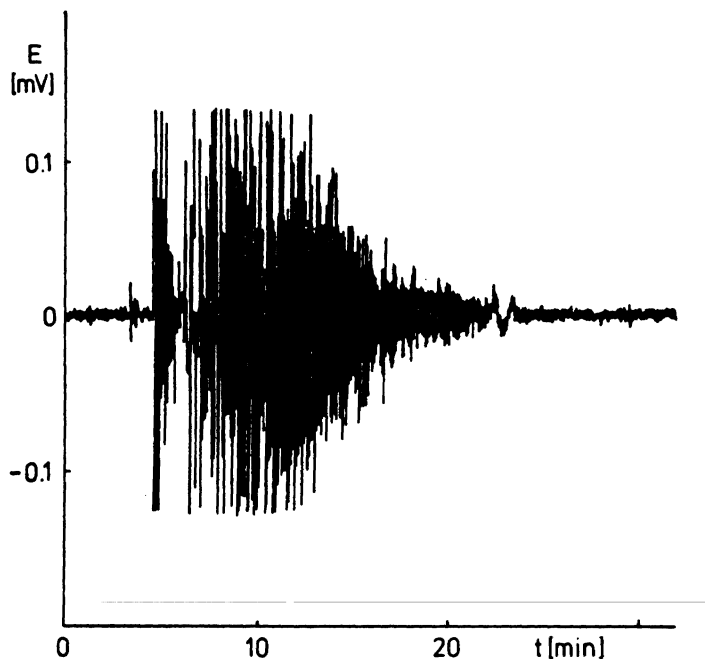
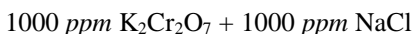


FIG. 5. Electrode noise output during single pit initiation and growth

activity which became less frequent as the experiment progressed and finally ceased altogether. The electrochemical noise output changed to a new type (Fig. 4).

The noise output of the electrode undergoing crevice corrosion appeared to be characterized by relatively long (1-24 h) "bursts" of very regular peaks occurring every 20-80 s. Examination of the electrode several days after this change revealed two small pits together with the start of crevice attack.



Prior to the chloride addition the mild steel electrode remained as "quiet" as described above, The first burst of noise was observed 20-30 s after the chloride addition, lasting some 10 min (Fig. 5). The d.c. potential decreased rapidly, ca 700 mV in the cathodic direction and after 100 s from the chloride addition a pit was observed on the electrode. After 4 min a cap of gelatinous product formed and the noise activity began to decay. The corrosion product then became brown and "powdery" and all noise activity ceased 10 min after the chloride ion addition.

The electrode was monitored for the next five days and although the cap increased in size no further noise activity was observed. On examination a single pit was found, approx. 1 mm in diameter and of a similar depth. No other corrosion was found on this electrode.

SUMMARY AND CONCLUSION

The results indicate that systems undergoing pitting or crevice corrosion may be monitored by sensitive measurements of the electrode potential, Pit initiation occurs

when the environmental conditions become aggressive, i.e. after chloride ion addition. Initiation continues as long as there are latent pit sites available.

Crevice corrosion progresses in well defined cycles, a rapid propagation stage followed by a longer interval of comparative inactivity. The crevice system appears to be very stable and the cyclic oscillations observed continued at a constant frequency over considerable periods of time. The data shows that crevice corrosion is a "preferred" process compared to pitting attack; once crevice attack begins then pit initiation ceases. This phenomenon has been generally observed in practice.

The results reported here have been duplicated on other systems undergoing these two forms of attack. Work is in progress to investigate the crevice oscillations in detail, using reference electrodes situated within the crevice. Long term measurements on various stainless steel electrodes are also being carried out.

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