An electrochemically integrated multi-electrode array namely the wire beam electrode (WBE) and noise signatures analysis have been applied in novel combinations to study crevice corrosion behaviour in the presence of pits. Characteristic electrochemical noise signatures were found to correlate with characteristic changes in WBE current distribution maps, which indicate corrosion rates distributions, corrosion patterns and the degree of pitting and crevice corrosion. Specifically, two characteristic noise patterns were observed: (i) the characteristic noise pattern of quick potential changes towards more negative direction with no recovery (termed noise signature I) was found to correspond with the initiation and stabilization of the anode inside crevice; and (ii) the characteristic noise pattern of the cyclic potential oscillation at a constant frequency (termed noise signature II) was found to correspond with the stable anodic dissolution in the occluded cavity site in WBE current distribution maps. A new parameter namely the localization parameter (LP) has been proposed to describe the degree of localization. The LP for crevice corrosion was found to be low compared to that for pitting corrosion.

1 Introduction

Localized corrosion, in the form of pitting and crevice corrosion are the most severe and the most commonly occurred in any engineering application. The difference between pitting and crevice corrosion is mainly in the initiation phase. Pitting initiates on an open surface and crevice corrosion occurs at an occluded site. The occlusion associated with a crevice provides a ready barrier to transport, so initiation of crevice corrosion is easier. Accelerated corrosion in a crevice can initiate at potentials well below the pitting potential, and after considerable periods of exposure with no prior evidence of crevice attack [1]. Pitting attacks are particularly susceptible to crevice corrosion, but many systems that show crevice attack do not suffer pitting on freely exposed surfaces. The highly corrosive micro-environment of crevices tends to be similar to the micro-environment established at the base of corrosion pits [2–5].

Despite major achievements made in the field of localized corrosion, such as pitting and crevice corrosion, some key questions remain controversial. For instance, there is insufficient understanding on the processes that lead to the breakdown of the passive film; that initiate the nucleation of a metastable pit; that cause pits to grow inside a crevice [1, 6–8]. Thus in order to understand the relation between mixed pitting and crevice corrosion, and a measure of the degree of localization a suitable monitoring tool has been a challenge to researchers. Traditional electrochemical techniques which are based on the Butler-Volmer equation such as the Tafel polarization method, the linear polarization method, cyclic polarization method and the AC impedance, in principle, are applicable only to measure the electrochemical kinetics of a uniform electrode surface [9]. Relatively new electrochemical techniques such as the scanning reference electrode (SRET) [10], the scanning Kelvin probe force microscopy (SKPFM) [11] have been applied as in situ techniques to map potential differences over an electrode surface and thus, localized corrosion patterns can be detected. These techniques, however, may not be suitable for monitoring of certain types of localized corrosion such as crevice corrosion.

Among the existing methods, the electrochemical noise signatures analysis has been employed to play a critical role in electrode noise origination [12, 13] the stochastic nature of localized corrosion including pitting corrosion [14–17, 19] and crevice corrosion [18, 19] and various mathematical models in understanding electrode potential and current fluctuations [20, 21], however, the exact origination process of electrochemical noise has not yet been clearly identified. The wire beam electrode (WBE) has been developed into an electrochemical sensor for monitoring various localized corrosion processes and it can measure the dispersion of current signals from the different electrodes and the degree of variations in the electrochemical properties among the electrodes [22–25].

The objective of this work is to better understand the crevice corrosion mechanism by correlating the noise signatures from localized attack with actual electrode processes based on the combined application of the WBE and noise signatures analysis. Carbon steel, the most widely used engineering alloy, has been selected to study in this work.

2 Experimental

The WBE is utilized in this work to study crevice corrosion because it could enable the direct correlation of noise activities to a specific location of the WBE surface. This investigation could help the establishment of an unambiguous correlation between electrochemical noise patterns and localized electrochemical corrosion processes.

Fig. 1 shows a typical experimental setup using the WBE-noise signatures method in the measurement of crevice corrosion with and without the presence of corrosion pits. A WBE made from 100 identical mild steel wires (0.18 cm in diameter) in which each wire was insulated using epoxy. The WBE

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was totally immersed in a corrosive electrolyte containing 0.017 M sodium chloride and 0.008 M sodium carbonate (Evans solution) under static conditions at 20°C to allow corrosion to occur. The WBE acts both as the mini-electrodes and as the corrosion substrates. The working area was approximately 2.25 cm² and the total metallic area was approximately 1.77 cm². The working surface of the WBE was polished with 400, 800 and 1000 grit silicon carbide paper and cleaned with de-ionized water and ethanol. The freshly polished WBE was positioned horizontal facing-up position and totally immersed in Evans solution at room temperature. A plastic semi sphere of about 2 cm diameter was placed on the WBE surface to create crevice area as shown in Fig. 1.

In order to measure potential and current distribution over the WBE surface the WBE wire terminals were connected to the computer cables using Autoswitch and AutoAC instruments. The WBE could enable the direct correlation of noise activities to a specific location of the WBE surface. The potential noise was obtained by measuring the open circuit potential of each wire of a WBE against a SCE reference electrode using a AutoAC and a computer controlled automatic switch device (Autoswitch). The WBE current distribution measurement over the WBE surfaces was done while concurrently monitoring potential noise of the electrodes. The maximum anodic current density (i_max), which has the largest positive current density value, the total anodic current density (i_tot), which is the sum of all the anodic current densities, and the number of anodes (N_a) were determined from a WBE current distribution map by registering in a data table for a WBE consisting of 100 wires.

3 Results and discussions

Firstly, pitting corrosion of mild steel was allowed to occur exposing to an Evans solution for 17 h and then crevice corrosion of the mild steel WBE experiment was continued by placing a semi plastic ball on the WBE to create a crevice, as described in Fig. 1. Fig. 2 shows typical electrode potential noise measured from the mild steel WBE surface after being exposed to the Evans solution for 300 h. The WBE current maps were measured concurrently with potential recording over the exposure period. The typical WBE maps showing the initiation, propagation and stable crevice corrosion are presented in Fig. 3. Three characteristic stages can be identified from the electrode potential record shown in Fig. 2(a) – Fig. 2(d):

(i) The first stage of corrosion

The first stage was characterized by a sharp drop in potential, shifting towards negative direction without recovery in Fig. 2(a). This type of noise behaviour is referred as noise signature I. The major pattern has been changed from pitting to crevice after about 1 h of exposure, which was demonstrated by WBE current distribution maps as shown in Fig. 3(a) and 3(b). WBE maps measured during the first stage show the initiation of major anode at wire no. 45 inside the crevice area after 1 h exposure, as shown in Fig. 3(c). The maximum galvanic current of the corrosion system, however, decreased from 0.436 mA/cm² to 0.385 mA/cm². Anodic potential within the crevice decreased from −440 to −530 mV which could be due to continued potential decrease in the crevice area with decrease in oxygen concentration.
Fig. 2. Time sequences of potential fluctuations obtained from a mild steel WBE during crevice corrosion.
Hladky and Dawson [14] first observed the change from pitting to crevice attack and they proposed that crevice corrosion is a preferred process compared to pitting attack and that once crevice attack begins then pit initiation ceases. It is generally believed that the initiation of crevice corrosion is originated by oxygen depletion in the small volume of a crevice. Before the initiation of crevice corrosion, anodic and cathodic reactions take place in and outside of a crevice. The noise signature I probably reveals the exact moment when massive anodic sites initiated under the crevice area.

(ii) The second stage of corrosion
The second stage of corrosion exposure was featured with the characteristic potential noise pattern of the continuous cyclic oscillations at a constant frequency as shown in Fig. 2(b) and 2(c). This type of noise behaviour is referred as noise signature II. WBE maps measured during this stage indicate that the propagation of crevice attack proceeded with the formation of new anodes in the crevice area. The first new stable anode became visible at wire no. 54 after 17 h immersion time as shown in Fig. 3(d). The second stable anode was found at wire no. 76 with the maximum galvanic current of 0.171 mA/cm² in Fig. 3(e). The third stable anode was found at wire no. 64 after 79 h as shown in Fig. 3(g). After 107 exposure, there were four stable anodes inside the crevice in Fig. 3(h) and they combined each other leading to the significant crevice area as indicated in Fig. 3(i). However, the maximum galvanic current was increased to 0.211 mA/cm², and later further decreased to 0.114 mA/cm².

Fig. 3a–e. WBE current (mA/cm²) distribution map obtained from a mild steel WBE showing the initiation, propagation and stable crevice corrosion after exposure to Evans solution for various periods.
Obviously in this experiment, the *noise signature II* was correlated with the successive and probably periodic formation of new stable anodes inside the crevice area as shown in Fig. 3(d)–3(g). Crevice progresses in well defined cycles, a rapid propagation stage followed by a longer interval of comparative inactivity [14]. The corrosion pattern became less localized with successive formation of anodes in the propagation stage.

(iii) The third stage of corrosion

The third stage of corrosion exposure was featured with electrode potential fluctuating randomly in a narrow range. As shown in Fig. 2(d), the electrode potential fluctuated within a narrow range of 15 mV over a 3-h period. WBE maps measured during this stage indicate continuous localized corrosion. During crevice propagation, no new pit appeared outside the crevice, on the other hand, the existing pit outside the crevice ceased as shown in Fig. 3(j). With the extension of the experiment, the maximum galvanic current value reduced six times (from 0.436 mA/cm² to 0.071 mA/cm²), indicating that the corrosion pattern became general after formation of a large anodic area inside the crevice. Corrosion proceeded in the whole occluded cavity site on the WBE by combination of the stable anodes and the crevice system appears to be very stable after 330 h.

The WBE sample undergoing crevice corrosion was kept in the Evans solution for 330 h. Instantaneous corrosion rate maps were used to determine total corrosion depths. This was achieved by summing up the corrosion depths over various periods of exposure to give a cumulative result [26]. Fig. 4 shows such calculated corrosion depth distribution map in Fig. 4(a) together with a microscopically observed corrosion depth map in Fig. 4(b) and a photo of the corroded WBE surface in Fig. 4(c) after exposed to corrosive environment for 330 h. The calculated total corrosion depths correlate quantitatively with the microscopically observed corrosion depths and the photo of the corroded WBE. This result confirms the accuracy of the corrosion measurement method.

In order to identify critical conditions for crevice corrosion to initiate, and parameters for stable localized anodes to grow, further analysis of the data has been carried out, mainly based on the calculation of a new parameter namely the localization.
parameter (LP). LP is designed to describe the degree of local- 
zation of corrosion based on the maximum anodic current 
density ($i_{\text{max}}$); the total anodic current density ($i_{\text{tot}}$); and the 
number of anodes ($N_a$):

$$LP = \frac{i_{\text{max}}}{i_{\text{avg}}}$$

(1)

where the average current density, $i_{\text{avg}} = \frac{i_{\text{tot}}}{N_a}$.

For localized corrosion systems, the current distribution is 
highly nonuniform, as a consequence, the maximum current 
density of the major anode becomes much higher than the av-
erage current density of all anodes and the larger the $LP$, the 
more localized the corrosion. The changes of $i_{\text{max}}$, $i_{\text{tot}}$, $N_a$ 
and LP of mild steel crevice corrosion in the presence of stable pits 
with immersion time in Evans solution for 300 h are shown in 
Fig. 5.

In the first stage of crevice corrosion, $i_{\text{max}}$, $i_{\text{tot}}$, and $N_a$ values 
increased during 24–50 h in Fig. 5(a), 5(b) and 5(c). Significant 
decrease in the localization parameter was observed as a 
result of more anode formation inside the crevice in Fig. 5(d). 
This is consistent with the fact that corrosion became more 
general.

In the second stage, fluctuation in values of $i_{\text{max}}$, and $i_{\text{tot}}$ was 
found during 50–330 h, as shown in Fig. 5(a) and 5(b). The 
fluctuation of current during this stage could be due to 
increased initiation and repassivation activities inside the cre-
vice. Continuous decrease in the localization parameter was 
observed, as shown in Fig. 5(d), during 50–330 h period. 
The change in localization parameter values shows that the 
degree of localization decreased when the system changes 
from highly localized pitting corrosion to less localized cre-
vice corrosion.

4 Conclusions

The WBE-noise signatures method has been developed and 
and applied successfully to study localized corrosion. The noise 
signatures have been found to be indicators of localized cor-
rosion initiation and propagation. For instance, the indicator 
for the initiation and propagation of crevice corrosion was 
found to be characteristic noise patterns I and II. The noise 
signature I was featured with quick potential changes towards 
more negative direction with no recovery and it was found to 
correspond with initiation of the anodes in crevice corrosion in 
the WBE map. The noise signature II was featured with the 
characteristic cyclic oscillations at a constant frequency and it 
was found to correspond with successive formation of stable 
anodes inside crevice area and the propagation of crevice cor-

Fig. 4. (a) Observed pitting and cre-
vice corrosion depth map, (b) calcu-
lated pitting and crevice corrosion 
depth map values (µm) and (c) the 
photograph showing a mild steel 
WBE surface after exposure to Evans 
solution for 330 hrs
rosion in the WBE map. The localization parameter has been proposed as an indicator for the degree of localization in localized corrosion. Continuous increase in the localization parameter indicates accelerated stable pit dissolution, while decrease in the localization parameter indicates more general corrosion or repassivation. The changes in localization parameter can be used to identify the stages of localized corrosion processes.

5 References


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