RESEARCH ARTICLE
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Monitoring Pitting Corrosion of Carbon Steel Using the Combined WBE-Noise Signatures Method

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ABSTRACT: An electrochemically integrated multi-electrode array namely the wire beam electrode (WBE) in combination with noise signatures analysis has been applied to study localized corrosion, especially pitting. The classic pitting corrosion of carbon steel in Evans solution was carried out by the correlation of electrochemical potential noise signatures and WBE current distribution maps. During carbon steel pitting corrosion process, the characteristic 'peak' of rapid potential transient, towards less negative direction, followed by recovery was found to correlate with the disappearance of unstable anodes leading to formation and propagation of stable anodes in WBE current distribution maps. Localized corrosion was the result of the anodic dissolution of the remaining anodic sites after disappearance of unstable anodes. This result suggests that the combined WBE-noise signatures method could be applied as a means of early detection and prediction of localized corrosion.

KEYWORDS: electrochemical method, electrochemical noise, the wire beam electrode, pitting, carbon steel.

INTRODUCTION

Localized corrosion is the most dangerous form of corrosion, and the monitoring and detection technique, which gives real-time indications of localized corrosion penetration rate, could be a highly desirable tool for engineering components in a localized corrosion environment. Despite major achievements made in the field of localized 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; and that terminate pits[1, 2].

Among the existing methods, the electrochemical noise method is the most promising technique for monitoring the stochastic nature of localized corrosion[3, 4, 5]. Two major applications of electrochemical noise analysis have been developed: the noise resistance method that was developed to determine general corrosion rates,[6, 7, 8, 9] and the noise signature method that was proposed to detect localized corrosion by recognizing characteristic noise patterns in the time domain[10] or in the frequency domain[3]. Although noise signatures have attracted the most interests due to the possibility of localized corrosion identification and quantification, their application still remains a rather controversial issue. One problem is the lack of proper experimental methods that could be used to directly correlate noise signatures to localized corrosion activities occurring at a specific location of an electrode surface. Another problem is that the exact origination process of electrochemical noise has not yet been clearly identified, although electrochemical heterogeneity has been recognized to play a critical role in electrode noise origination[11, 12] and various mathematical models have been employed in understanding electrode potential and current fluctuations [13, 14, 15].

The objective of this work is to better understand the localized corrosion mechanism by correlating the noise signatures from localized attack with the actual electrode process based on the combined application of the wire beam electrode (WBE) and noise signatures analysis. The key strategy of this work is to employ a multi-piece electrode system namely the WBE[8, 16, 17, 18, 19]. If localized corrosion initiates on a WBE surface due to local breakdown of the protective surface film, a sudden potential change could occur at locally broken areas. Although such event may only result in small fluctuations in overall electrode potential, it could result in significant local potential fluctuations that can be detected using a WBE. The addressable multi-electrode structure allows a WBE to measure local galvanic current distribution. For this reason, the sensitivity of noise detection could be improved. This investigation could help the establishment of an unambiguous correlation between electrochemical noise patterns and localized electrochemical corrosion processes.

MATERIALS AND METHODS

This experimental method is a new technique in that WBE is applied in conjunction with the potential noise signatures. The experimental design is illustrated in Figure 1. The investigated carbon steel was UNS no. G10350 with the composition of 0.31 - 0.38% C, 0.6 - 0.9% Mn, <0.04% P, <0.05% S and 98.63 - 99.09% Fe. The WBE acted both as the mini-electrodes and as the corrosion substrates. The WBE was fabricated from 100 wires by embedding wires in epoxy resin. The carbon steel wire was 0.18 cm in diameter. The working area of the carbon steel WBE was approximately 3.24 cm^2 (1.8 cm ´ 1.8 cm) and the total metallic area was approximately 2.54 cm^2. The working surface of the WBE was polished with 400, 800 and 1000 grit silicon carbide paper, and cleaned with deionised water and ethanol before being positioned in a horizontal facing-up position. The working surface was totally immersed in the corrosive electrolyte under static conditions at air-conditioned room temperature (about 20 °C) to allow pitting corrosion to occur. The corrosive solution was Evans solution (0.017 M NaCl + 0.008 M Na_2CO_3 solution). The solution was prepared with deionized water and analytical grade reagents.

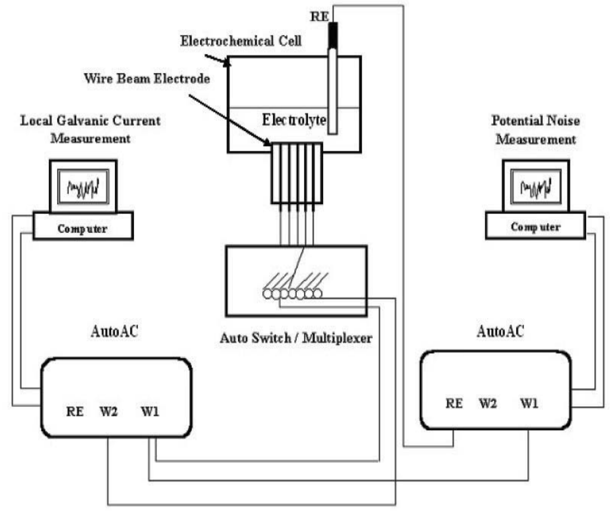

Fig 1. Schematic diagram showing an experimental set-up for detecting potential noise over a WBE and for mapping galvanic currents flowing into/out of each wire in the WBE from pitting corrosion system.

The corrosion potential distribution was obtained by sequentially measuring the open circuit potential of each wire against the reference electrode (SCE) using the AutoAC and AutoSwitch. Potential noise recording

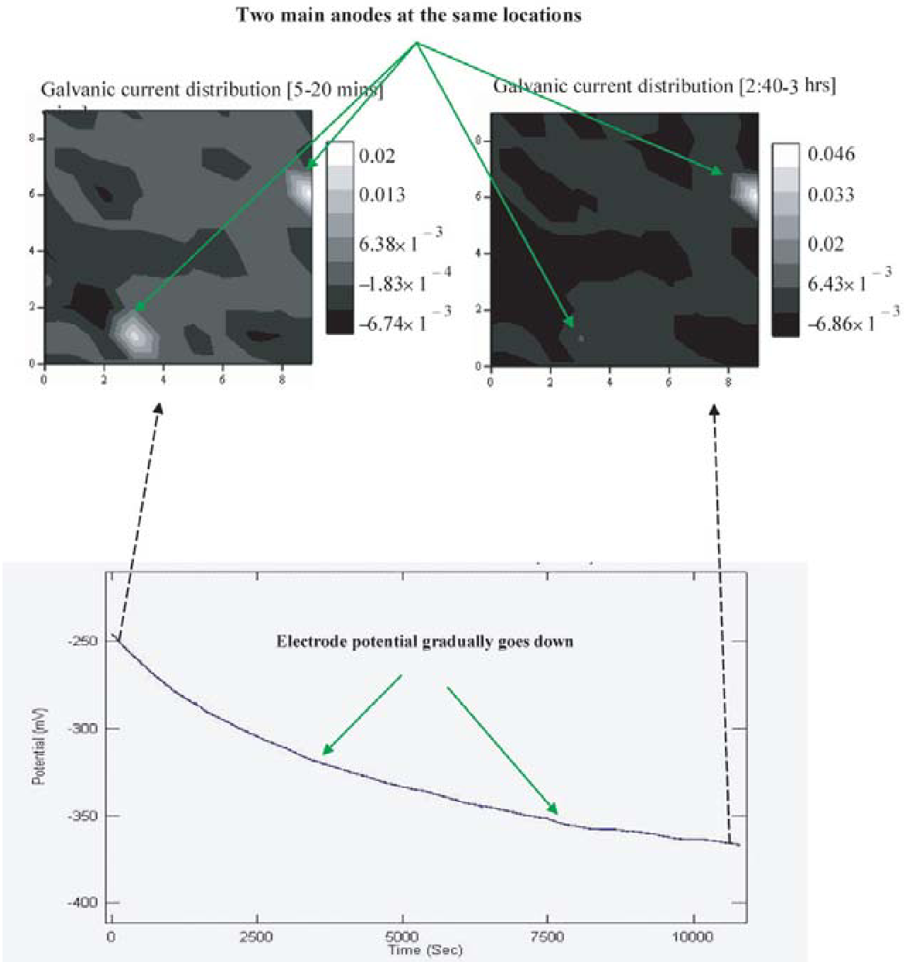

Fig 2. Correlation of potential noise signature and galvanic current (mA/cm^2) distribution map obtained from a carbon steel WBE showing the first stage prior to pitting after exposure to Evans solution for 3 hours.

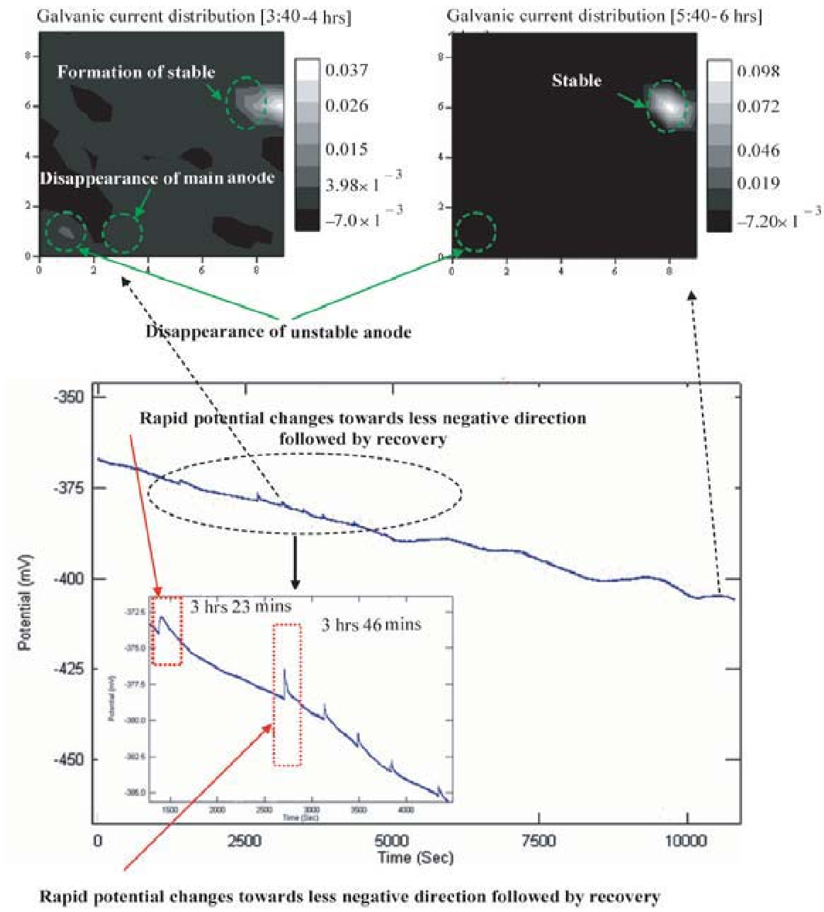

Fig 3. Correlation of potential noise signature and galvanic current (mA/cm^2) distribution map obtained from a carbon steel WBE showing pitting initiation, repassivation and stable pit formation stage after exposure to Evans solution for 6 hours.

was conducted immediately after the WBE was immersed in the test solution with a data sampling rate of 2 data/second, and the recording was continuous over the whole test period. The galvanic currents flowing between each individual wire and the wire beam system were measured by sequentially inserting the AutoAC between a chosen wire terminal and all other terminals shorted together using the AutoSwitch. The measurement duration for each pair of wire was 10 seconds with sampling rate of 10 points/sec, and a current distribution survey of the whole electrode surface was completed in about 17 minutes. Current or potential values measured from each wire of WBE (I_k and E_k, k = 1-100) were plotted using Mathcad environment (Mathcad Professional &, MathSoft, Inc., Massachusetts, USA) to produce a WBE current distribution map. There are a total of 100 data points in a WBE current distribution map and the x and y scales of the WBE current distribution map represent the dimensions of the WBE. The vertical grey bar shows the galvanic current density values. A positive current value indicates an anodic dissolution current, while a negative current value indicates a cathodic reaction current.

Corrosion rate maps measured after different periods of exposure were used to calculate total corrosion depths over the whole experimental period since this corrosion rate distribution gives the instantaneous corrosion dissolution rate of the metal at the particular point in time. This was achieved by summing the calculated corrosion depths after various periods of exposure to give a cumulative result. A simplified method of corrosion rate calculation used in this work has been described in detail[8]. Visual observation of pit morphology and pit depth measurement was carried out using an optical microscope Nikon Epiphot 200 (magnification from 50× to 1000 ×) to confirm the calculated corrosion depth data from WBE experiment.

Results and Discussion

Figure 2 presents typical electrode potential noise measured from a carbon steel WBE surface after being exposed to the Evans solution. WBE current distribution maps over carbon steel WBE surface were measured simultaneously with potential recording over exposure periods of 9 hours. Three characteristic stages were observed from the electrode potential noise record shown in Figures 2-4.

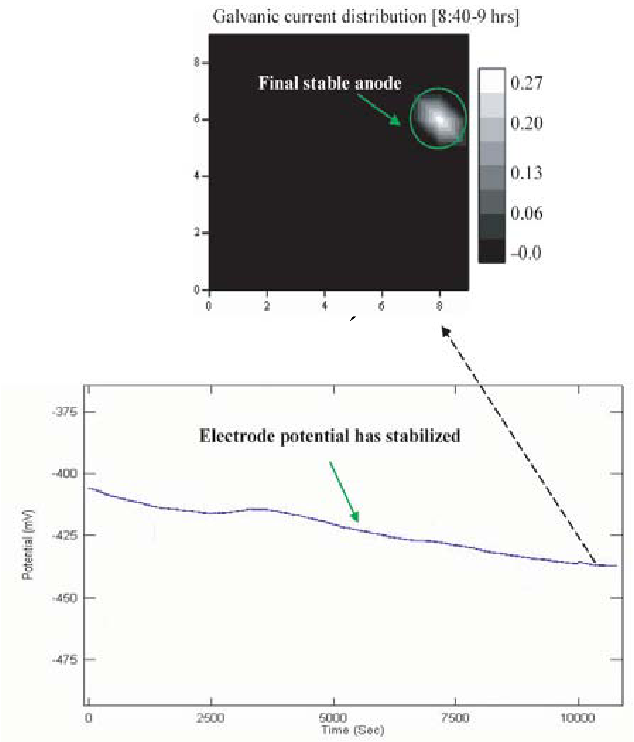

Fig 4. Correlation of potential noise signature and galvanic current (mA/cm²) distribution map obtained from a carbon steel WBE showing stabilization stage of pitting after exposure to Evans solution for 9 hours.

Initial Stage

The initial stage prior to pitting was characterized by gradual potential shifting towards negative direction. The potential of carbon steel was observed, as shown in Figure 2, to fall continuously from an initiate potential of approximately -250 mV to –350 mV in 3 hours. After this initial period, only two significant anodes remained at location of wires no. 31 and no. 84 in the WBE current distribution maps. The maximum anodic current density of these anodes was gradually increased from 0.02 mA/cm^2 to 0.046 mA/cm^2. The electrode potential shifting was mostly likely due to continued decrease in anodic potential. Since the major cathodic reaction in the corrosion system should have remained steady and oxygen reduction and the concentration of oxygen was controlled by diffusion from the air, the potential of cathodic area should have remained stable. The major increase in galvanic currents between anodic and anodic zones must be due to a decrease in potential in the anodic zone. Corrosion pattern was localized even in this early stage of corrosion.

Pit Initiation and Repassivation Stage

The pit initiation and repassivation stage was featured with the characteristic 'peak' of rapid potential transient, towards less negative direction, followed by recovery as shown in Figure 3. This electrode noise pattern was reported in many pitting corrosion systems[10, 15, 20]. This noise signature became visible after 3 hours 23 mins and 3 hours 46 mins of exposure. During this stage, the WBE current distribution maps measured from the WBE surface in Figure 3 showed that the existing main anode at wire no.84 disappeared after 3 hours. At the same time, the growth of the main anode at wire no.31 was also observed. The anodic area at wire no.31 was gradually expanded, and then the main anode position shifted to the nearest neighbouring wire no.32. The maximum galvanic current of this main anode was further increased to 0.098 mA/cm^2 after 6 hours exposure. The formation of new anodic site at wire no.82 was observed at 3 hours 46 minutes and this unstable anode was repassivated within 20 minutes as shown in Figure 3. The characteristic 'peak' of rapid potential transient, towards less negative direction, followed by recovery represented pit initiation and repassivation stage and this stage was found to correspond with the disappearance of unstable anodes. The corrosion pattern became more localized during this stage after the disappearance of some minor anodes.

Stabilization Stage of Pitting

The stabilization stage of pitting was featured with electrode potential fluctuating randomly in a narrow range as shown in Figure 4. The fluctuated electrode potential was 20 mV over a 3-hour period. WBE maps measured during this stage showed further growth of the main anode at wire no. 31 and the formation of a new major anode at wire no. 32. A major anode at location of wire no. 32 became stabilized and continued rapid anodic dissolution with the galvanic current of 0.279 mA/cm^2 after 9 hours immersion period as shown in Figure 4. The pitting corrosion pattern became highly localized with the extension of exposure time.

Calculated Corrosion Depth and Corroded Surface

The carbon steel pitting experiment in Evans solution was carried out for 17 hours. The pit depth distribution map over the corroded WBE surface was as shown in Figure 5(a). Optical microscopes (Nikon Epiphot 2000 and Nikon Epiphot 200) were used to measure pit depth measurement. The calculated pit depth distribution in Figure 5(b) showed the pit depth of 8-10 mm. The photograph of the corroded WBE surface was as shown in Figure 5(c). There is a good correlation between the maps and the photograph.

Conclusions

The wire beam electrode (WBE) has been applied for the first time in a novel experimental set-up to simultaneously measure electrode potential noise and WBE current distribution maps for direct comparison

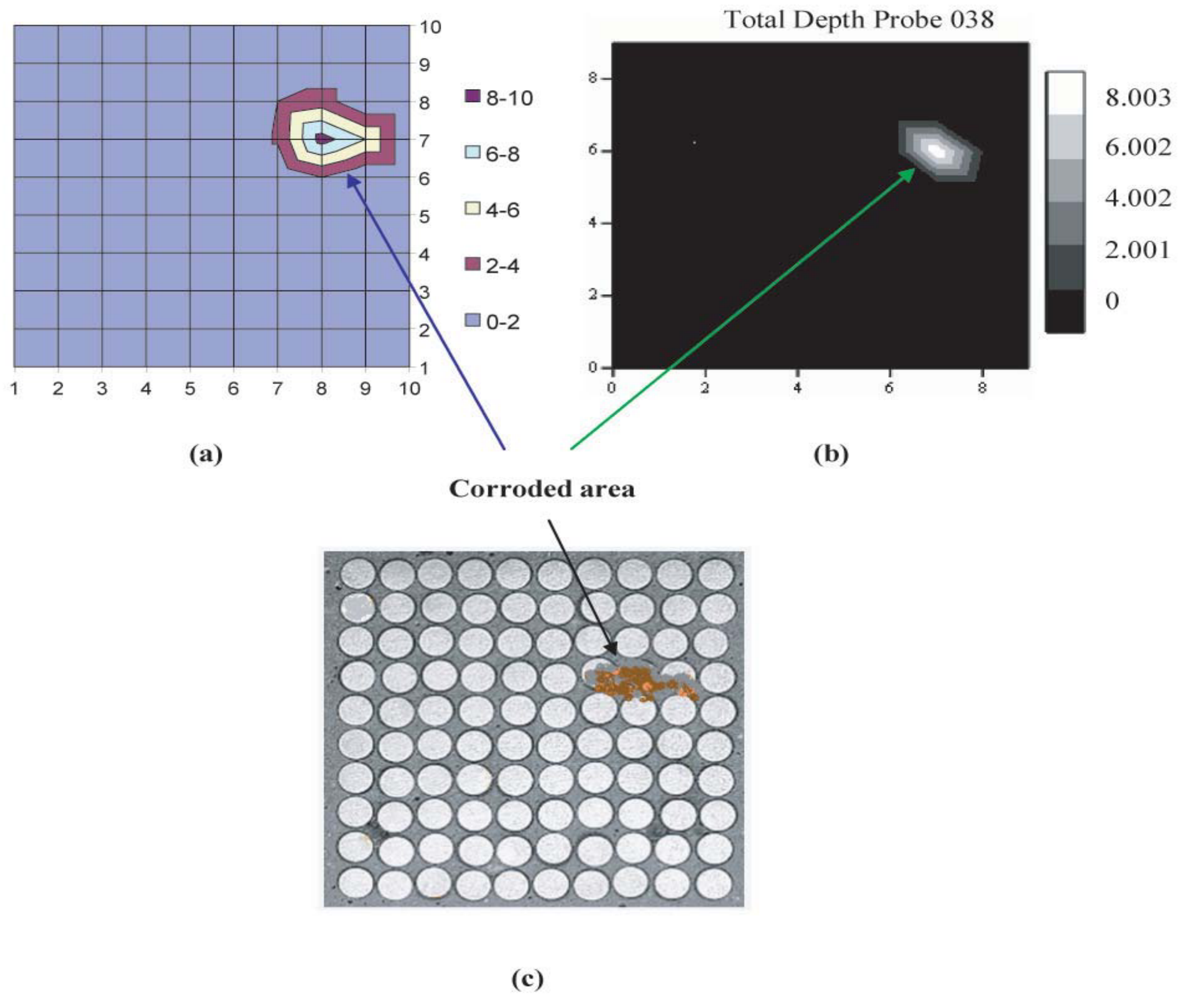

Fig 5. (a) Observed pitting corrosion depth map, (b) Calculated pitting corrosion depth map values (in mm) and (c) the photograph showing a carbon steel WBE surface after exposure to Evans solution for 17 hrs.

and correlation of electrode noise and corrosion behaviour. Experiments have been carried out using carbon steel WBE in Evans solution. Correlation between characteristic patterns in noise signatures and corrosion behaviour has been observed. More specifically, the characteristic sharp peaks of rapid potential transient, towards less negative direction, followed by recovery was found to correlate with the disappearance of unstable anodes in WBE current distribution maps. This result suggests that, the number of active anodes in the carbon steel pitting corrosion system was small, and that electrode noise activities were associated with the disappearance of unstable anodic sites, which lead to the formation and propagation of stable anodic site from the existing major anode.

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