Chiang Mai J. Sci. 2005; 32(3) : 521-527
www.science.cmu.ac.th/journal-science/josci.html
Contributed Paper

# A Novel Sensing Technique for Monitoring Pitting Corrosion of Stainless Steel Type 316L

**Naing Naing Aung* and Yong-Jun Tan**

Corrosion Laboratory, School of Materials Science and Engineering, Nanyang Technological University, Nanyang Avenue, Singapore 639798

*Author for correspondence, e-mail: p115573@ntu.edu.sg

## ABSTRACT

A novel electrochemically integrated multi-electrode array namely the wire beam electrode (WBE) in combination with noise signatures analysis has been designed to monitor pitting corrosion of one of the best corrosion resistance ferrous alloys, stainless steel type 316L. From the direct correlation of electrochemical potential noise signatures and galvanic current distribution maps during pitting corrosion processes, two characteristic noise patterns were observed prior to stable pit formation: (i) the characteristic 'peak' of rapid potential transient, towards less negative direction, followed by recovery (termed *noise signature I*) was found to correlate with the disappearance of unstable anode; (ii) the characteristic noise pattern of quick potential changes towards less negative direction followed by no recovery (termed *noise signature II*) was found to correspond with the massive disappearance of minor anodes leading to formation of highly localized major anodes in the galvanic current distribution maps.

**Keywords:** electrochemical method, electrochemical noise, pitting corrosion, stainless steel, the wire beam electrode.

## 1. INTRODUCTION

Pitting corrosion usually occurs on the passivated metal due to local weakness of the passive film and often leads to catastrophic failure because it is generally quite unpredictable with regard to the time of initiation. Knowledge about the pitting mechanism is therefore the prime necessity in order to protect such a serious corrosion problem for the engineering application of passive alloys. Among the existing electrochemical corrosion monitoring techniques, the electrochemical noise analysis is the most promising method to study the localized corrosion which has been regarded as a random (stochastic) phenomenon coupled to deterministic kinetics and potential and current noises [1]. Several researchers who have been studying the application of noise signatures to the identification of pitting mechanism usually only tried to relate certain characteristic noise features to pits those are identified visually or microscopically after experiment is completed [2-9]. The WBE [10, 11] can measure the significant local potential fluctuations and instantaneous local galvanic current distribution [12]. The objective of this work is to better understand pitting mechanism by correlating the noise signatures from localized attack with actual electrode process based on the combined application of the WBE and noise signatures analysis.

## 2. MATERIALS AND METHODS

The laboratory tests were carried out applying stainless steel type 316L WBE and the experimental setup was as shown in Figure 1. The WBE acts both as the mini-electrodes

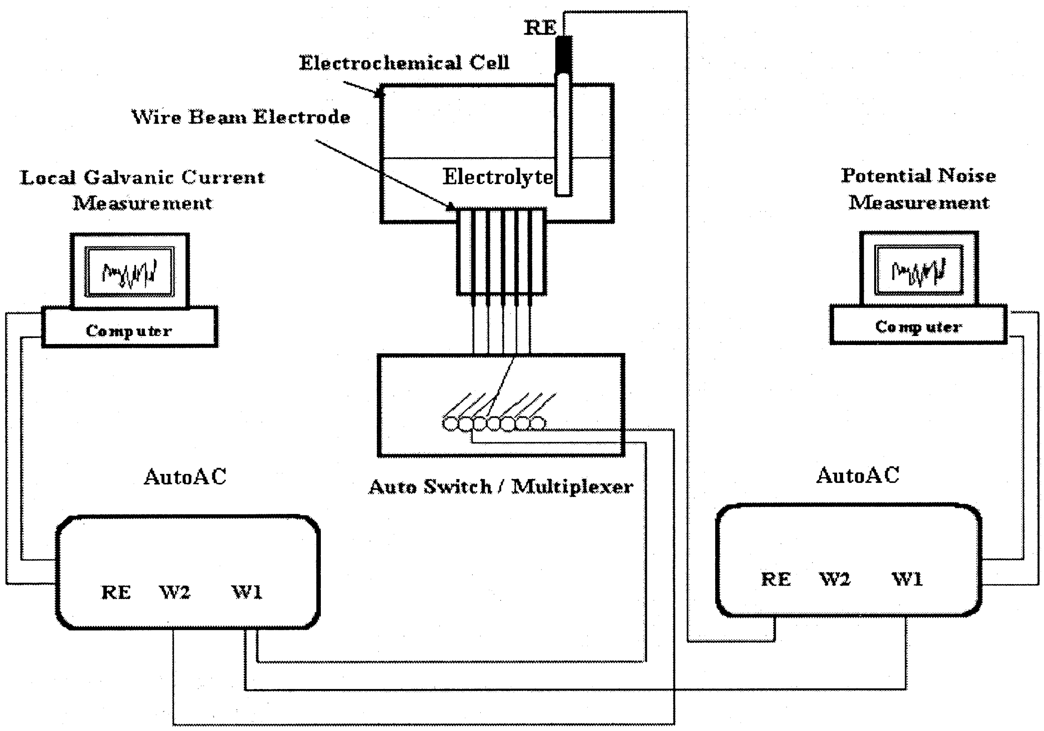



**Figure 1.** Schematic diagram showing an experimental set-up for detecting potential noise over a WBE and also for mapping galvanic currents flowing into/out of each wire in the WBE from pitting corrosion system.

and as the corrosion substrates. The WBE was fabricated from 100 wires by embedding wires in epoxy resin. The stainless steel wire had a diameter of 0.15 cm and the working area was approximately 2.25 cm$^2$ (1.5 cm × 1.5 cm). The working surfaces of the WBE were polished with 400, 800 and 1000 grit silicon carbide paper and then it was cleaned with deionised water and ethanol before being positioned horizontal facing-up position. The working surfaces were totally immersed in the 6% $FeCl_3$ solution under static conditions at air-conditioned room temperature (about 20 °C) to allow pitting corrosion to occur. The potential noise was obtained by measuring the open circuit potential of each wire of a WBE against an SCE reference electrode using a AutoAC and a computer controlled automatic switch device (Autoswitch). The galvanic current distribution measurement over the WBE surface was done while concurrently monitoring potential noise of the electrodes. An automatic zero resistance ammeter (AutoZRA, ACM Instruments, England) was connected in sequence between a chosen individual wire terminal and all other terminals shorted together using the Autoswitch to measure galvanic currents. Corrosion rate maps measured after different periods of the 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. A simplified method of corrosion rate calculation used in this work has been described in detail [13]. Optical microscopes (Nikon Epiphot 2000 and Nikon Epiphot 200) were used to measure pit depth measurement.

## 3. Results and Discussion

First Stage Noise Signature before Pitting

The first stage of pitting was characterised by gradual potential shifting towards negative direction. Galvanic current maps were measured simultaneously with potential recording for 20 min intervals. It can be seen that corrosion anodic sites existed at the very beginning of electrode exposure to the corrosion environment (Figure 2). The maximum anodic current density increased significantly from 0.94 – 2.166 mA/cm$^2$ during 3 h exposure. The continuous shifting of electrode potential towards negative direction was obviously not due to increase in anodic area, since the anodic area did not change much during the first 3 h. Legat *et al.* [14] also observed the same noise signature after immediate immersion in stainless steel pitting system. After correlating the potential noise signature and galvanic current distribution maps, it was clearly demonstrated that the passive film on SS316L surface was etched with corrosive electrolytes within 20 min and that performed anodic sites at more active areas.

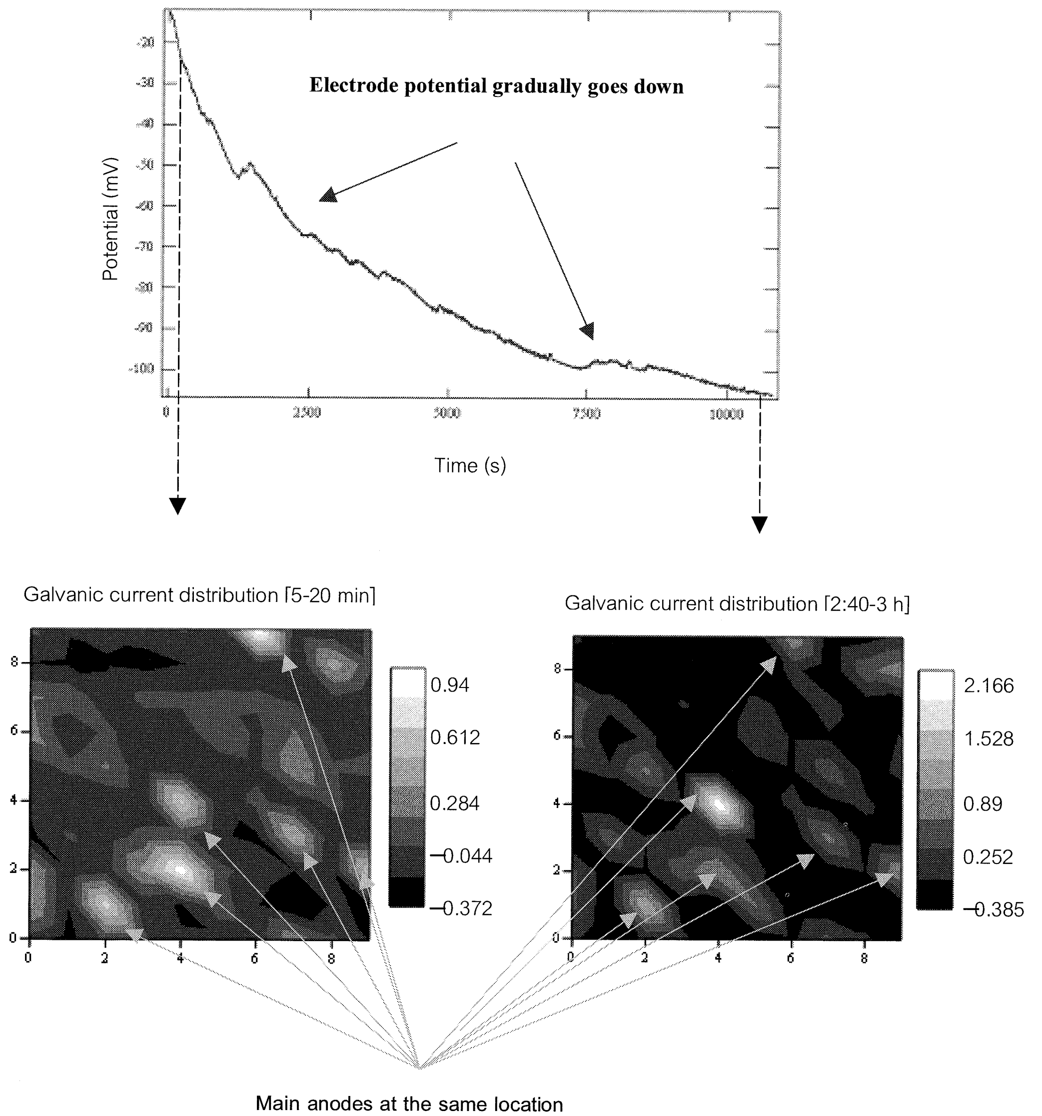



**Figure 2.** Correlation of potential noise signature and galvanic current (mA/cm$^2$) distribution map obtained from a stainless steel WBE showing the random distribution of anodes and cathodes after exposure to 6% $FeCl_3$ solution for 3 h.

### 3.1 Noise Signature from Pit Initiation and Repassivation

After 6 h exposure, pitting initiation and repassivation was featured with a characteristic 'peak' of rapid potential transient, towards less negative direction, followed by recovery (*noise signature I*) as shown in Figure 3. This electrode noise pattern has been reported in carbon steel and stainless steel pitting systems [2, 6, 8]. However so far there is no evidence to explain this pattern. In this particular experiment, it was observed no new anode was formed; instead one anode disappeared. This transition between active and passive states would be possible only during state when the mass transport limitation is not sufficient to form the stable anode. This result suggests that the origin of *noise signature I* was not the conventionally believed passive film rupture process, but the anode disappearance process. The disappearance of a major anodic site lead to decrease in anodic area and thus it caused a sudden shift of electrode potential toward less negative direction.

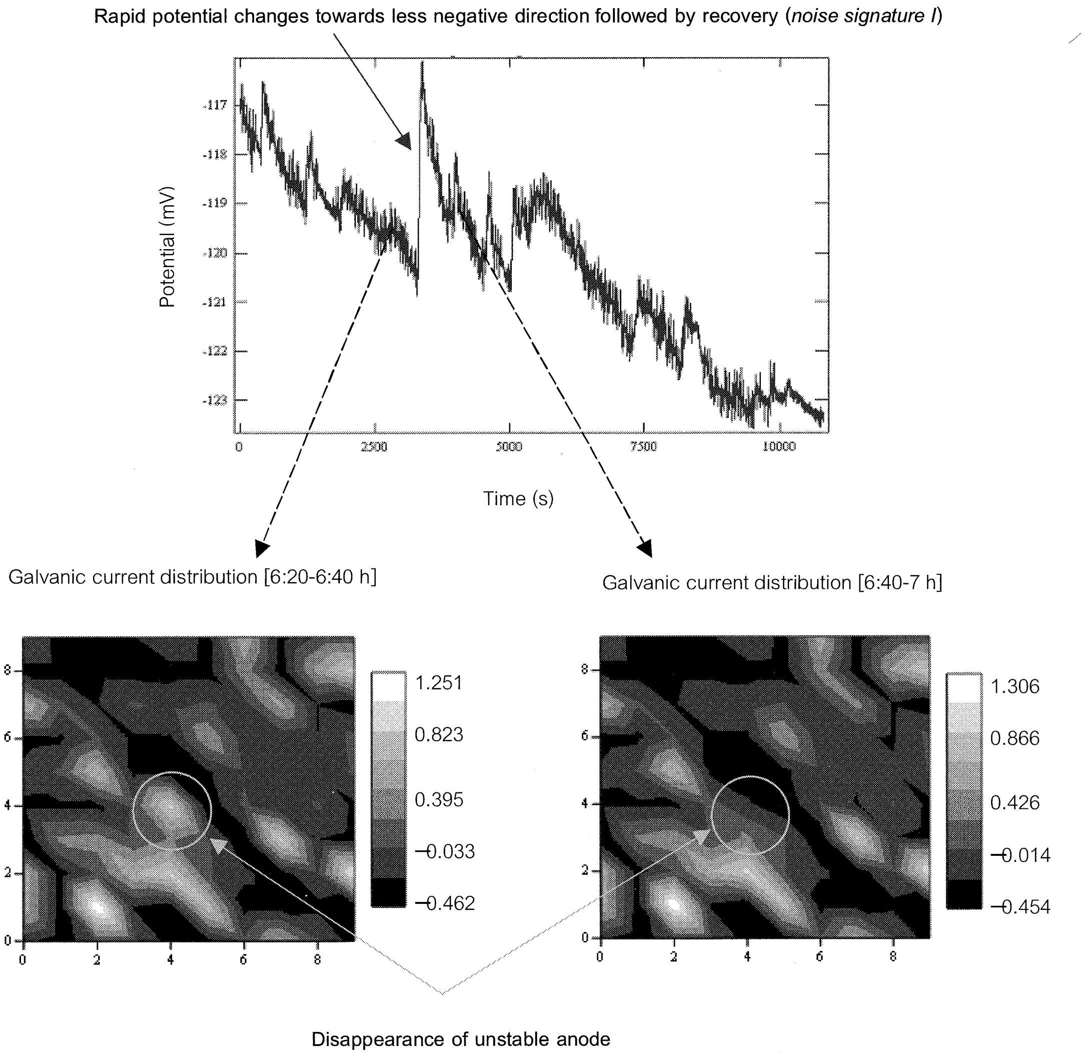



**Figure 3.** Correlation of potential noise signature and galvanic current ($mA/cm^2$) distribution map obtained from a stainless steel WBE showing disappearance of unstable anode after exposure to 6% $FeCl_3$ solution for 9 h.

### 3.2 Noise Signature from Stable Pit Formation

The stable pit formation was featured with the characteristic pattern of rapid potential transient towards less negative direction followed by no recovery (*noise signature II*). As shown in Figure 4, the *noise signature II* became visible after 87 h of exposure. It was corresponded with the massive disappearance of minor anodes leading the localized stable major anode in the galvanic distribution maps. This process has lead to the formation of a major stable anode at location of wire no. 35 and two other smaller anodes in the stainless steel WBE. The galvanic current of the stable anode was further increased from 3.05 mA/cm$^2$ to 3.418 mA/cm$^2$. Sato [15] has related the limit of

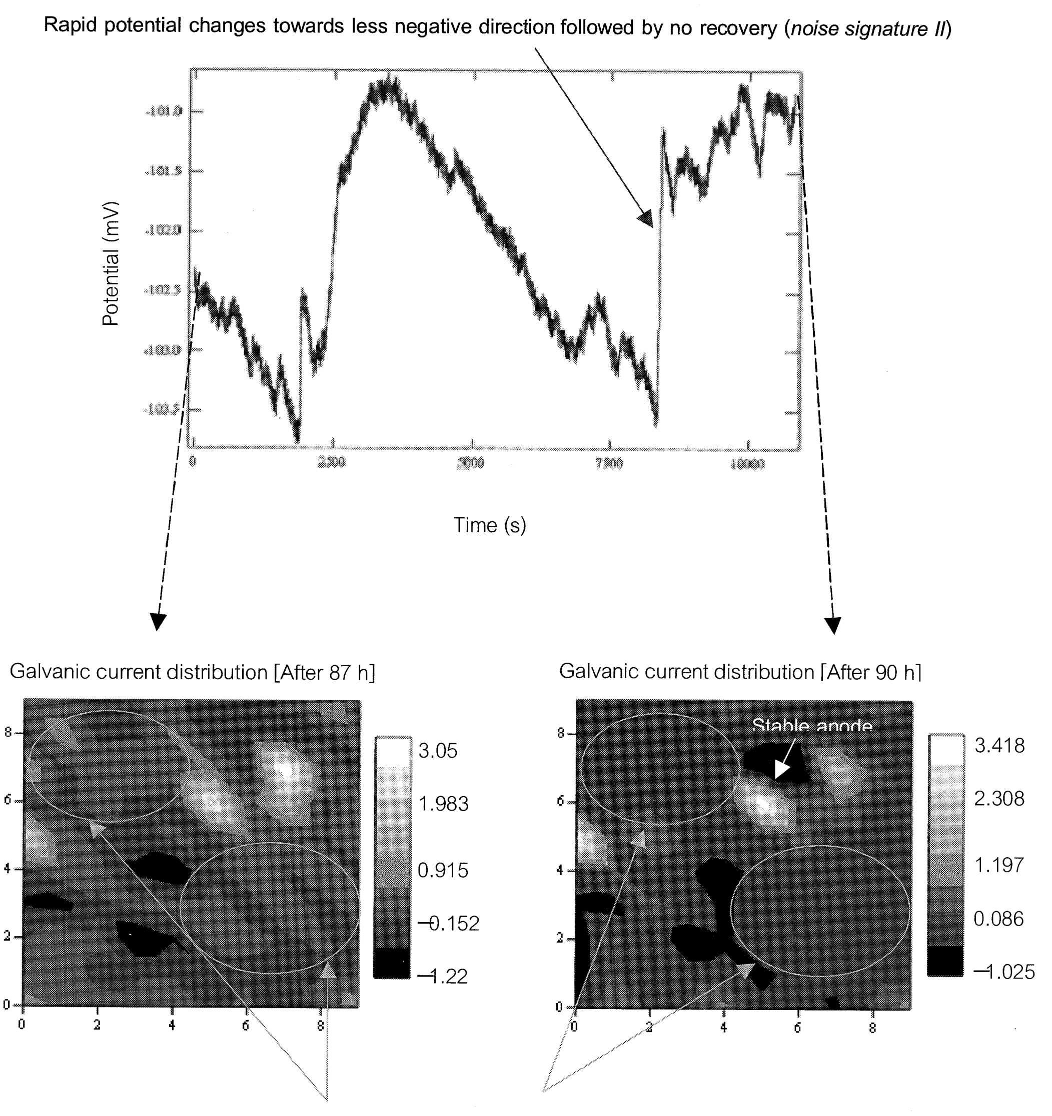



**Figure 4.** Correlation of potential noise signature and galvanic current (mA/cm$^2$) distribution map obtained from a stainless steel WBE showing massive disappearance of anodes leading to stable anode formation after exposure to 6% $FeCl_3$ solution for 90 h.

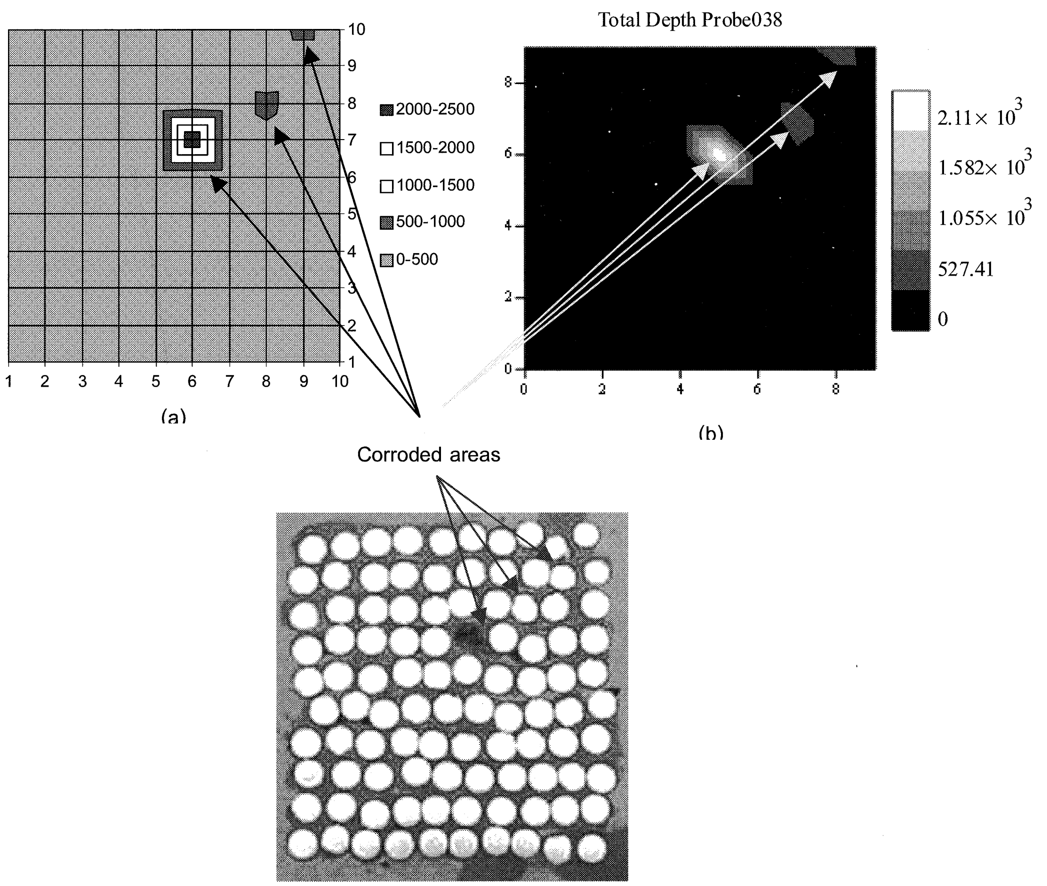
the stability of dissolution of pits to the etching-brightening transition, stable pits can grow as soon as brightening occurs. If his explanation is true, the *noise signature II* should be corresponding with the brightening stage of the stable anode. As expected, the stainless steel major anode at wire no. 35 became the stable anode.

### 3.3 Stabilization of Pitting

The pitting stabilization was featured with electrode potential fluctuating randomly in a narrow range. The stabilized and continued rapid anodic dissolution of major anode was observed at the location of wire no. 35 of stainless steel WBE. After 240 h exposure, the galvanic current was already 11.686 mA/cm².

### 3.4 Calculated Corrosion Depth and Corroded Surface

The stainless steel WBE sample undergoing pitting was kept in the 6% $FeCl_3$ solution for 240 h. The maps showing pit depth distribution over the corroded WBE surfaces were shown in Figure 5(a), together with pit depth map in Figure 5(b), was calculated by accumulating anodic dissolution over the whole duration of exposure. The maximum depth was approximately 2000 – 2500 μm. 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.




(c)

**Figure 5.** (a) Observed pitting corrosion depth map, (b) Calculated pitting corrosion depth map values (μm) and (c) the photograph showing a stainless steel WBE surface after exposure to 6% $FeCl_3$ solution for 240 h.

## 4. 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 and correlation of electrode noise and corrosion behaviour. Experiments have been carried out using a stainless steel Type 316LWBE exposed to a solution containing $FeCl_3$. The *noise signature I*, which was observed during initiation and repassivation stage of pitting corrosion, was featured with the disappearance of unstable anodic site in the galvanic current distribution maps. The *noise signature II* was found to correspond with the massive disappearance of anodic sites leading to accelerated major anodic dissolution. This work suggests that the WBE method could be used in combination with the noise signatures to achieve early recognition, detection and prediction of localized corrosion.

## REFERENCES

[1] Kearns J.R., and Scully J.R. Editor(s), Electrochemical Noise Measurement for Corrosion Applications, ASTM STP 1277, ASTM, p. ix, 1996.

[2] Hladky K., and Dawson J.L., The Measurement of Localized Corrosion Using Electrochemical Noise, *Corros. Sci.*, 1981; **21**: 317-322.

[3] Bertocci U., Mullen J.L., and Ye Y.X., Electrochemical Noise Measurements for the Study Localised Corrosion and Passivity Breakdown; In M. Fromet (Edn.), Passivity of Metals and Semiconductors, Elsevier Sci. Pub., Amsterdam, 1983.

[4] Williams D.E., Fleischmann M., Stewart J., and Brooks T., Some Characteristics of the Initiation Phase of Pitting Corrosion of Stainless Steel; In M. Duprat (Edn.), Electrochemical Methods in Corrosion Research, Materials Sciences Forum 8, Trans. Techn. Pub., Suisse, 1983.

[5] Okada T., A Theoretical Analysis of the Electrochemical Noise during the Induction Period of Pitting Corrosion in Passive Metals: Part 1. The Current Noise Associated with the Adsorption/Desorption Processes of Halide Ions on the Passive Film Surface, *J. of Electroanalyti. Chemist.*, 1991; **297**: 349-359.

[6] Tan Y.J., Lowe A., Kinsella B., and Bailey S., Analysis of Electrochemical Noise Using Fourier Transform, Maximum Entropy and Wavelet Methods, Proc. ACA Corrosion & Prevention 98, Australia, 1998.

[7] Cheng Y.F., and Luo J.L., Passivity and Pitting of Carbon steel in Chromate Solutions, *Corros. Sci.*, 1999; **41**: 4795-4804.

[8] Smulko J., Darowicki K., and Zielinski A., Detection of Random Transients Caused by Pitting Corrosion, *Electrochimi. Acta*, 2002; **47**: 1297-1303.

[9] Fukuda T., and Mizuno T., The Evaluation of Pitting Corrosion from the Spectrum Slope of Noise Fluctuation on Iron and 304 Stainless Steel Electrodes, *Corros. Sci.*, 1996; **38**: 1085-1091.

[10] Tan Y. J., *U.S.A. Pat. No.* 6132593, 2000.

[11] Lunt T.T., Brusamarello V., Scully J.R., and Hudson J.L., Interactions among Localized Corrosion Sites Investigated with Electrodes Arrays, *Electrochem. and Solid-State Lett.*, 2000; **3**: 271-274.

[12] Tan Y.J., Wire Beam Electrode: A New Tool for Studying Localized Corrosion and Other Heterogeneous Electrochemical Process, *Corros. Sci.*, 1999; **41**: 229-247.

[13] Tan Y.J., Bailey S., Kinsella B., and Lowe A., Mapping Corrosion Kinetics Using the Wire Beam Electrode in Conjunction with Electrochemical Noise Resistance Measurements, *J. Electrochem. Soc.*, 2000; **147**: 530-539.

[14] Legat A., and Zevnik C., The Electrochemical Noise of Mild and Stainless Steel in Various Water Solutions, *Corros. Sci.*, 1993; **35**: 1661-1666.

[15] Sato N., The Stability of Pitting Dissolution of Metals in Aqueous Solution; In R.P. Frankenthal and F. Mansfeld (Edn.), Corrosion and Corrosion Protection, The Electrochemical Society, Pennington, 1981: 101-111.