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Research Paper

Determination of pitting corrosion stage of stainless steel by galvanodynamic impedance spectroscopy

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ABSTRACT

This paper investigates the methodology for differentiation of multistep process of pitting corrosion of AISI 304 stainless steel in the environment of iron (III) chloride. Measurements were performed using Galvanodynamic Electrochemical Impedance Spectroscopy (GDEIS). Application of this methodology allowed monitoring of natural corrosion process without external current ($I_{DC} = 0A$) nor potential perturbation of the system. Applied sinusoidal AC current does not influence significantly registered DC potential. Analysis confirms that it is possible to distinguish all stages of pitting corrosion: passive state, metastable state, initiation of pitting, active pitting corrosion state. Characteristic potential oscillations related with pitting corrosion were detected. Research shows that GDEIS method can be with success utilized in the monitoring of pitting corrosion.

1. Introduction

Pitting corrosion is one of the major threat for technical performance of industrial plants due to its localized character and autocatalytic mechanism. Monitoring of this type of corrosion is important part in Risk Base Investigations. Nowadays there are many different solutions for pitting corrosion monitoring. Non destructive testing methods have the highest application in industrial environments. Ultrasonic technique (UT) allows observation of the size and shape of pits. Unfortunately, only advanced stage of pitting corrosion can be spotted by this method due to low sensitivity. Local character of damage requires large number of measurements for accurate diagnosis [1–3]. Another popular pitting corrosion monitoring technique is acoustic emission method [4–6]. Acoustic signals are generated by hydrogen bubbles evolution or cracking of passive layer [7]. The main advantage of this technique is possibility of recording early stages of pitting corrosion due to degradation process of passive layer [8]. The high quality results are obtained for materials characterized by thick passive layer like aluminum and magnesium alloys [9]. Different characteristics of acoustic signals allow distinction of the type of corrosion process [10]. Acoustic emission method despite many significant advantages is rarely applied in on-line corrosion monitoring systems due to high sensitivity on external noise which is common in industrial environment. Optical Fibres (OF) method is another approach in pitting corrosion monitoring. Measuring system is consisted of laser and fibre transmitting signal on the surface of exposed metal. Analysis is done by photodiodes. Changes in the stress conditions on the surface due to the corrosion activity change also the stress conditions of the optical fibre. The changing stress conditions of the optical fibre modulate the light pulse. Selective and nondestructive way of measurement are the most important features in detection of corrosion threat by this method [11,12]. Unfortunately there is a problem with distinction of pitting corrosion from other corrosion processes. Electrochemical noise (EN) method is gaining increasing attention in the field of electrochemical monitoring methods. This method is nondestructive but similarly to the OF technique, differentiation of pitting corrosion from general corrosion is difficult. Also, due to low value of current and potential signals this method is sensitive for background noise especially in industrial conditions [13–15]. The simplest monitoring method is measurement of open circuit potential [16]. The value of potential describes thermodynamical state of the working electrode. Differentiation of active and passive state of the metal is possible. The measurements are characterized by limited selectivity which will be precisely described in the results and discussion part.

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Table 1
Chemical composition of stainless steel 304 type.

C	Si	Mn	P	S	Cr	Ni
0.05%	0.65%	1.5%	0.03%	0.01%	18.1%	8.1%

The aim of this work is presentation of novel pitting corrosion monitoring method based on Dynamic Electrochemical Impedance Spectroscopy (DEIS). Presented method allows studies of the kinetics of pitting corrosion processes in the conditions without external potential or temperature perturbation in the galvanostatic mode. DEIS method is extension of the commonly used Electrochemical Impedance Spectroscopy (EIS) [17]. Important feature of the proposed method is possibility of on-line investigation of the dynamic electrochemical systems. As an example this method allowed research on the passive layer cracking process due to tensile stress [18–20]. DEIS method was also implemented in the probability assessment of the pitting corrosion occurrence in magnesium [21]. An essential extension of previous studies is the use of galvanostatic mode in DEIS measurements where direct current is kept on the zero level.

2. Experimental

Electrochemical measurements were carried out in three-electrode system, where working electrode was austenitic stainless steel 304 type (AISI). Chemical composition of the material is listed in the Table 1.

Area of working electrode was equal to 1 cm^2. The reference electrode was Ag/AgCl and counter electrode was platinum mesh. Measurements were conducted in the $FeCl_3$ solutions with varied concentration: 1.500%, 0.750%, 0.562%, 0.375%, 0.281%. Solution were stabilized by hydrochloric acid with concentrations suggested by ASTM G48 norm. $FeCl_3$ solutions were significantly lower than standard 6% iron (III) chloride due to too high corrosion aggressiveness of this solution. Increasing concentration enhance the corrosion aggressiveness of the solution. Preliminary electrochemical measurements in the form of cyclic polarization according to the norm G61 (ASTM) were conducted in order to indicate possibility of occurring pitting corrosion for each concentration. This measurements were made using Gamry Reference 600 device. Polarization was conducted in the anodic direction up to 2,5 V potential vs. open circuit potential (OPC) with 1 mV/s rate. The highest value of current didn't exceed 10 mA.

The main measurements were conducted using Galvanodynamic Electrochemical Impedance Spectroscopy (GDEIS). Implementation of this novel measuring technique was motivated by dynamic features of pitting corrosion process. The issue is illustrated on Fig. 1 in the form of recorded corrosion potential for 304 stainless steel exposed to 0,750% $FeCl_3$ conducted using Gamry Reference 600.

In 0,750% $FeCl_3$ environment autocatalytic process of pitting corrosion occurs. Corrosion process has multistep character. As the consequence significant changes of recorded potential in time in the form of oscillations and fluctuations were observed. Dynamic character of changes exclude application of classical electrochemical impedance spectroscopy technique. In such a case obtained spectra would tend to be averaged. This phenomena can be observed in Fig. 1. Oscillations of the potential in the time of several seconds reach even 100 mV. In the light of above utilization of potentiostatic mode is impossible, because working electrode would be subjected to high polarization. In this paper galvanodynamic electrochemical impedance spectroscopy is proposed as a methodology for characterization multistep process of pitting corrosion, taking place in the environment of iron (III) chloride.

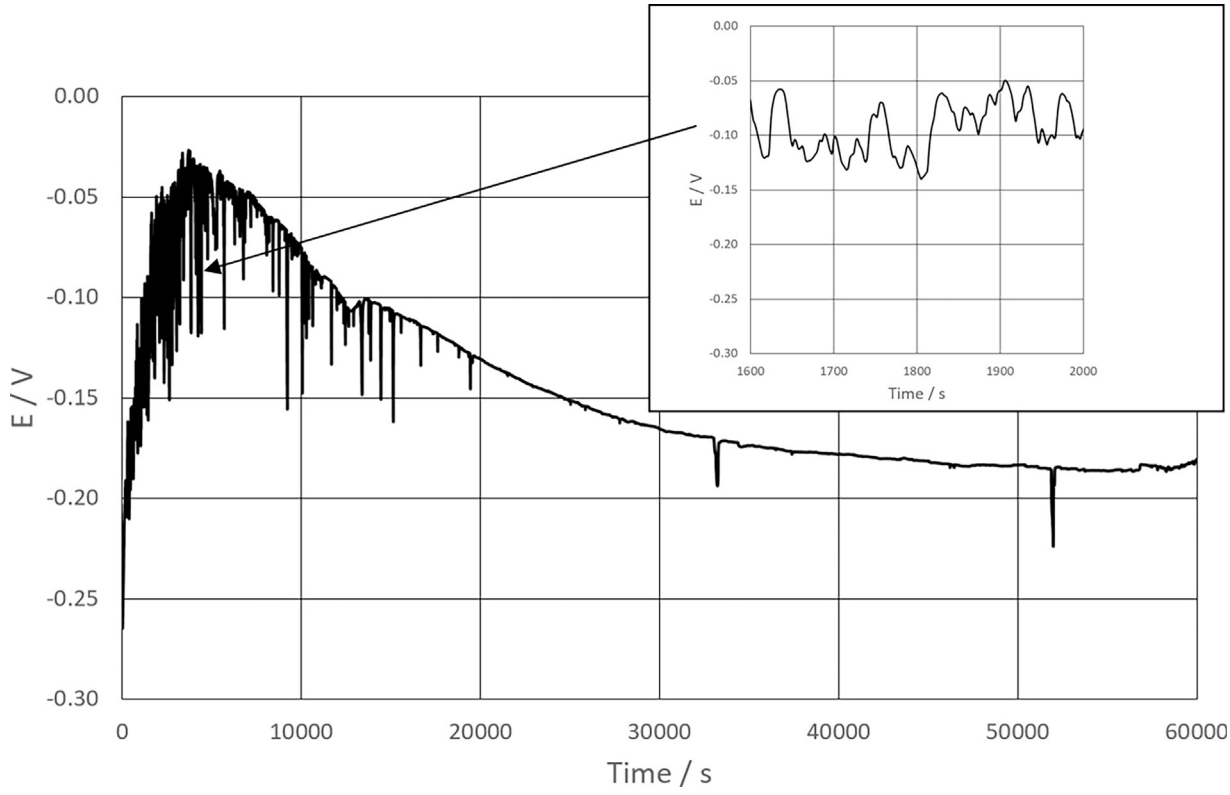

Fig. 1. Corrosion potential of 304 stainless steel exposed to 0,750% $FeCl_3$.