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Quantitative evaluation of pit sizes for high strength steel: Electrochemical noise, 3-D measurement, and image-recognition-based statistical analysis

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ABSTRACT

In this study, pit depths, diameters, and locations of high strength X80 pipeline steel in aerated sodium chloride solutions are quantitatively investigated by electrochemical current noise (ECN) measurements as well as confocal laser scanning microscopy (CLSM). From the results obtained via ECN signals and SEM images, pits are believed to be initiated immediately, and current transients are strongly affected by the cathodic process. The computer simulation of ECN reveals that overlapping processes lead to both increase and decrease of transient amplitude depending on the time delay of original transients. Furthermore, the pit sizes estimated from the current transients are far lower than the actual pit sizes observed from SEM images. Hence, current transients obtained from ECN correspond to nucleation instead of the propagation process of pits. An image recognition technique is introduced for the purpose of recognizing corrosion pits from optical images, which significantly increases the efficiency of statistical analysis of pit diameters and pit locations. Results obtained from the statistical analysis of high strength pipeline steel in aerated NaCl solutions indicate that pit diameter follows lognormal distribution, and pit sites are completely spatial random.

1. Introduction

Recently, high strength steel has been intensively used widely within the construction of large-volume, high-pressure long-distance pipelines for meeting the increasing demand of oil and gas. However, most of the onshore and offshore pipelines are located in harsh environment, such as in the presence of CO_2/H_2S, chloride ion, bacteria, and stress. Most of these pipelines are susceptible to pitting corrosion [1–3] and stress corrosion cracking [4,5]. Because of the special chemical composition of high strength steel, its corrosion behavior could be different from those of other materials [6–8]. In our previous study, the pitting corrosion of high strength steel in an aerated NaCl solution has been systematically investigated [9], which filled the research gap of the corrosion of high strength steel in marine environment. Severe pitting corrosion and unique large pit morphology were observed. However, the severity and distribution of pitting could not be quantitatively evaluated by traditional electrochemical methods and microscopic observation.

Standard methods for the quantitative evaluation of pitting corrosion include visual inspection, nondestructive inspection, mass loss measurement, pit depth measurement by vertical sectioning through a pre-selected pit, pit rating on the basis of standard charts, and statistical analysis based on manual counting [10]. However, these methods are typically inconvenient and time-consuming. For example, it is almost impossible to measure the depths of all pits by vertical sectioning; manually counting the number of pits is also extremely tedious and inefficient. In addition, none of these methods can simultaneously measure the pit density and pit locations accurately.

As compared with the other microscopic observation methods such as optical microscopy [11,12], scanning electron microscopy (SEM) [13], and atomic force microscopy (AFM) [14], confocal laser scanning microscopy (CLSM) can provide rapid, accurate, non-contact measurements of surface topography in three dimensions. This technique was developed in the 1980s [15]. Since then, it has been widely applied in several areas such as biological research [16], material science [17], and food research [18]. The strong ability of 3D measurement makes it an excellent tool for the quantitative analysis of pit shape.

Electrochemical noise (EN), which involves the measurement of self-generated potential and current fluctuations, can provide useful information about the nature of pitting corrosion. The perceived advantages of EN over the other electrochemical techniques make it become increasingly popular for studying pitting corrosion [19]. There are also some studies on the quantitative evaluation of pitting corrosion using ECN. Guo [20] has found that the intergraded current based on wavelet transform can be applied to quantitatively evaluate pitting corrosion

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and pitting corrosion inhibition. The nucleation rate, average amplitude, and average lifetime were estimated from ECN signals by integrating the current, which were useful for the evaluation of inhibition efficiency. The integrated results of current were found to be consistent with those obtained from EIS. The power spectral, statistical, wavelet analyses, and chaos theory were also used to investigate the uniqueness of the parameters proposed for the identification of various types of corrosion processes [21–23]. Zhou has also reported that [24] noise resistance is useful for quantitatively evaluating the corrosion rate for general corrosion. However, the reliability of ECN signals for evaluating the sizes of corrosion pits has not been discussed in these studies. Guan [25] has reported that the current transients may not be reliable for quantitatively measuring the pit sizes for the Al–Mg–Si alloy.

In this paper, ECN and CLSM are used for the quantitative investigation of the pitting corrosion of high strength pipeline steel in aerated NaCl solutions. The ability of ECN for quantitatively estimating pit sizes is also analyzed by simulating the overlapping process of current transients. For decreasing the difficulty of statistical analysis, an image recognition technique is introduced for the automatic detection of corrosion pits from microscopic images. Pit diameters and locations are accurately recognized and written into an array, which makes the statistical analysis of pit distribution rapid and convenient. The distribution characteristics of pit diameters and pit locations for high strength steel in aerated NaCl solutions are discussed.

2. Experimental setup

2.1. Materials and electrolyte

The material used in the experiment was X80 pipeline steel, having chemical composition as shown in Table 1. The stress–strain curve of the as-received X80 steel was obtained on a tensile tensing machine. According to the tensile test, the yield strength (σ_s) and the tensile strength (σ_b) of X80 steel were determined as 647.0 MPa and 772.8 MPa, respectively.

A three-electrode configuration was used for the measurement of electrochemical current noise (ECN). The experimental specimens were machined from steel plate, soldered to copper wires and mounted with epoxy resin leaving a circular working area of 0.5 cm^2 with a corresponding working area diameter of 0.8 cm. Before immersion into the electrolyte, the working area of the specimen was ground with 400–1200-grit waterproof abrasive paper, polished with 6 μm diamond polishing film, and then cleaned with distilled water and acetone. The electrolyte used is an aqueous 0.05 mol/L NaCl solution. The pH of the sodium chloride solution was adjusted to 4 with hydrochloric acid and sodium hydroxide. The reference electrode was a saturated calomel electrode (SCE), connected with the electrolyte through a salt bridge positioned close to the working electrode surface in order to minimize ohmic potential drop. A Pt wire was used as the counter electrode. All the electrodes and probes were fixed in a 1 L flask, which had an open mouth connecting the electrolyte with the atmosphere. The temperature of the system was controlled at 25 ± 1 °C in a water bath.

2.2. Electrochemical measurement

Electrochemical current noise (ECN) at open circuit potential was measured with an electrochemical workstation (CS350, Wuhan Corrtest Instrument Co., Ltd., China), and the data was recorded with Corrtest software. After the working electrode was immersed into the electrolyte, the ECN signal was recorded immediately with a sampling rate of 50 Hz. The ENTOOLS software was used to analyze the ECN signal.

2.3. Morphology observation

Each specimen was ground gradually with 400–1200-grit waterproof abrasive paper and cleaned with distilled water and acetone. Then the specimens were immersed in 0.05 mol/L NaCl solutions for 1 h. Two groups of tests in the NaCl solutions with $pH = 4$ and 7 were conducted separately to investigate the influence of solution pH on the pitting morphology. The pitting morphology was observed using scanning electron microscope (S-3000N, Hitachi, Japan), and confocal laser scanning microscope (LEXT OLS4000).

2.4. Pit detection algorithm

A program was written for automatically detecting circles (pits) in an optical image of pitting corrosion using the image processing toolbox in Matlab. The locations and diameters of all pits were determined by this program. The pit detection process is explained as below.

For near-circular pits in corrosion images, pit recognition entails circle finding, which is a classical topic in the image processing field. Several algorithms have been proposed for automatically detecting the diameter and location of circles in image [26,27], and studies are still ongoing [28]. In this paper, a simple algorithm based on the "imfindcircles" function in Matlab is used for the recognition of circular pits in images. The recognition of circles using this function consists of several steps: import the image, convert the imported image into a gray image, set the possible range of radius, set the parameters (such as the "subject polarity" and "sensitivity"), and draw the detected circles on images. Depending on the size and magnification of image, the algorithm is capable of detecting the smallest pit diameter. For an image with a size of 1024 × 1024 pixels and a magnification of 5, the smallest pit diameter that can be detected is approximately 10 μm (5 pixels). The algorithm is capable of detecting a small pit diameter for an image with high magnification. However, usually low magnification is used to obtain more pits in one image. The largest pit radius (approximately 50 pixels) is 10 times the smallest pit radius (about 5 pixels). Image noise affects the accuracy of pit detection. Images with high contrast and few scratches are required to obtain a high recognition accuracy.

Actually, several advanced algorithms are available for the detection of circles. For example, a more powerful algorithm based on the Hough transform is capable of detecting circles with a wide radius range, high accuracy, and strong ability for distinguishing between circles and irregular shapes (noises) [29]. They are not discussed in this paper and may be presented in future studies.

2.5. Statistical analysis

The pit diameter histogram was fitted by Minitab 17. The spatial point pattern analysis of pit location was finished using the 'spatstat' library, which is a powerful package in R language for the analysis of spatial point pattern [30].

Table 1
Chemical composition of X80 by wt.%.

Steel	C	Si	Mn	P	S	Ni	Mo	Cu	V	Al	Nb	Ti	Fe
X80	0.07	0.30	1.77	0.02	0.005	0.22	0.21	0.22	0.06	0.06	0.05	0.021	Bal.