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Effects of inhomogeneous elastic stress on corrosion behaviour of Q235 steel in 3.5% NaCl solution using a novel multi-channel electrode technique



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ABSTRACT

In-situ corrosion characterization of Q235 steel under inhomogeneous elastic stress in 3.5% NaCl solution was investigated by zero resistance ammeter and electrochemical noise techniques combined with a newly developed multi-channel working electrode and reference electrode system. The galvanic corrosion, resulted from the so-called stress cell with the higher stress locations as anodes relative to the low stress locations, could be induced by the applied inhomogeneous elastic stress. The distribution and intensity of anodic and cathodic areas in galvanic corrosion were shown to be a function of corrosion time. The effect of corrosion products on the corrosion behaviour was also discussed.

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1. Introduction

Ships and marine structures are usually subjected to the combined effects of mechanical and electrochemical actions when they are in service, and the stress caused by welding, machining, cold working and operating force etc. is also inevitable [1,2]. The both mechanical effect and chemical effect interacting with each other can accelerate the failure of structural components. This synergistic effect has been defined as the mechanochemical effect (MCE) [3,4]. In this case, localized corrosion such as galvanic corrosion resulted from the so-called stress gradient cell, in which the higher stress locations become anodic to the lower stress locations, may occur on the steel plate with a stress gradient or inhomogeneous stress distribution. Since localized corrosion can cause serious damage to marine structures, it would therefore be of significance to study the electrochemical response of the steel plate to the inhomogeneous stress distribution. In addition, it is noteworthy that most of the stress level on structural surface should not be too high, but should be in the elastic range of steel to meet the safety design of marine structures [2].

Some researchers [5,6] have reported on the influences of elastic stress on the electrochemical corrosion, and it was concluded that the mechanoelectrochemical dissolution could not occur in the elastic region. Xu et al. [7] also investigated the effect of uniaxial elastic stress on corrosion behaviour of X100 pipeline steel in a near-neutral pH solution, and it was concluded that the static elastic stress did not affect the corrosion potential. However, many researchers [1,8-15] have found that elastic stress could cause negative shift of corrosion potential and accelerate corrosion of steel significantly. In such a condition, stress gradient cells can form on the steel plate with stress gradient, and then cause the significant dissolution of the metal in relatively high stress area. As mentioned above, although the problems caused by the interactive effects of mechanical stress and electrochemical corrosion are very serious, the intrinsic relations between them still remain not thoroughly understood [4]. In addition, previous researchers generally focused on the effect of mechanical stress on general corrosion behaviour and missed studying the MCE more deeply to gain the useful information on the effect of inhomogeneous stress distribution on the localized corrosion process.

Traditionally the evaluation of localized corrosion relies largely on weight-loss measurement, visual and microscopic examination and surface analysis through various surface analytical techniques [16,17]. Electrochemical noise (EN) technique has also been extensively used for detecting and evaluating localized corrosion

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[18,19]. Recently, Sakairi et al. [20] employed the EN technique to investigate the effects of various metal cations on galvanic corrosion behaviour of A5052 aluminum alloy in low chloride ion containing solutions, and it was found that both current and potential fluctuations from electrochemical noise could show a good correlation in evaluating pitting incubation and initiation. Although these methods have provided valuable information for evaluating localized corrosion, it should be noted that the use of a single specimen has some limitations in evaluating the spatial distribution of actual localized corrosion [16,17,19,21].

The approach of overcoming this disadvantage is the use of a multi-channel probe or multi-channel electrode technique which can acquire spatial and temporal information related with localized corrosion processes [17,22]. Fujimoto et al. [23] studied the susceptibility of type-304 stainless steel in 3.5% NaCl solution to crevice corrosion by employing a 10-channel reference electrode, and eventually the generation of crevice corrosion was successfully detected. Tan et al. developed the wire beam electrode (WBE) technique by employing the electrochemically-integrated multichannel electrode array and applied this technique to mapping and estimation of localized corrosion [17,19,24], inhomogeneous corrosion under organic surface films [25] and solid deposits [26] and also pitting corrosion of bare electrode caused by electrode inhomogeneity and electrochemical heterogeneity [27]. Fushimi et al. [22] employed the multi-channel electrode technique to study galvanic corrosion on carbon steel welded with type-309 stainless steel, and Naganuma et al. applied this technique to crevice corrosion of iron [16] and to the crevice corrosion of four kinds of stainless steels used in a salt manufacturing plant [21]. Recently, Sato and Azumi [28] also employed the similar technique to monitor the coupling current map of the iron partially covered with Zn coating in a simulating atmospheric environment. The advantage of the multi-channel electrode technique is able to effectively and continuously measure in-situ the potential of each channel electrode and participating electronic current flowing between electrodes to each other in the metallic phase, and thereby to distinguish the distribution of anodic and cathodic locations, their intensity and time-transition [17,22,24].

Inhomogeneous stress distribution is almost inevitable for marine structures in actual environmental conditions, and meanwhile corrosion is also a major factor inducing the age-related structural degradation [29–31]. Therefore, for the steel plate subjected to inhomogeneous stress, it is necessary to study the MCE more deeply to achieve a more precise corrosion rate assessment so as to guarantee the structural strength and lifetime prediction accuracy. The major objective of present study is to investigate the effects of inhomogeneous elastic stress on corrosion behaviour of Q235 steel plate in an aerated 3.5% NaCl solution by employing zero resistance ammeter (ZRA) and electrochemical noise (EN) techniques, combined with a newly developed multi-channel electrode system in which the Q235 steel plate was divided into multiple working electrodes, rearranged in epoxy resin to reproduce the original shape of the steel plate, loaded with their respective mechanical stress and integrated to an electronic circuit through relay switches. This enables simultaneous in-situ monitoring of participating current and corrosion potential of each working electrode through a multi-channel reference electrode technique, and thereby the distribution of anodic and cathodic sites under practical corrosion conditions can be determined. This multi-channel electrode system also has advantages in its simple devices and extensive applicability to immersed corrosion system subjected to external mechanical stress. It is anticipated that some concluding remarks achieved in this study will provide practical insights into the effects of inhomogeneous elastic stress on the corrosion process of actual marine structures.

Table 1 Chemical composition of the Q235 steel specimen.

Element	С	Si	Mn	P	S	Fe
Content (wt.%)	0.182	0.045	0.15	0.017	0.016	Balance

2. Experimental procedures

2.1. Material and specimen preparation

Test specimens were cut from a Q235 steel plate with the chemical composition as shown in Table 1. The yield and tensile strengths as well as the elongation at break of the tested steel are 245 MPa, 410 MPa and 25%, respectively, and the yield-strength ratio is 0.6.

The specimens were machined into two types of geometry [7], i.e., the specimen with equal cross-section (ES specimen) and the specimen with continuous variational cross-section on its central portion (VS specimen). The size of ES specimen was $150 \text{ mm} \times 120 \text{ mm} \times 2 \text{ mm}$. The VS specimen (referring to Fig. 1a) was used to generate a non-uniform stress distribution along its midline direction by applying constant tensile loads on both ends. Prior to test, all the specimens were first ground with silicon carbide papers to 1000 grit and then thoroughly cleaned by dehydrated ethanol, and finally dried in air. Fig. 1b presents the structure of ES specimen with two glued strain gauges and four welded metallic lead wires (ca. 0.46Ω in each wire resistance) electrically connected with steel surface. The strain gauges were first glued by cyanoacrylate glue (Simultaneous Taiwan Enterprise Co., model 502) to the steel surface and subsequently their upper surfaces were coated with silicone rubber (Kafuter K-703) for waterproof sealing. The area of the specimen exposed to solution was kept invariant and equal to $90 \, \text{mm} \times 10 \, \text{mm}$, and the other parts were covered with epoxy resin (Alteco Chemical Pte Ltd, model 3 ton-4 min) for waterproof sealing so as to prevent non-test parts of the specimen from

Six pieces of ES specimens used as working electrode (WE) were loaded with various levels of mechanical stress through a loading experimental apparatus (Fig. 1c) respectively and in sequence, and then were numbered consecutively in the order of stress level from #1 with the highest stress level to #6 without mechanical stress. The six pieces of WEs were subsequently integrated to an electronic circuit and immersed together in test solution for electrochemical measurements.

2.2. Loading method

A three-point bending method was adopted to exert constant tensile stress on the working surface of each WE. Fig. 1c shows a schematic diagram of the three-point bending experimental apparatus with six threaded rods. Different stress levels can be obtained by adjusting the adjustable threaded rods. The value of the applied stress was accurately measured by the strain gauges embedded in each WE. In order to ensure adequate stress gradient between WEs, the stress levels applied to different WEs were enough distributed, and they were 0 MPa, 70 MPa, 100 MPa, 130 MPa, 160 MPa, and 190 MPa (below the yield strength of Q235 steel), respectively.

2.3. Experimental measurements

The electrochemical test was carried out in a transparent plastic box, which was used as an electrochemical cell, and the cell was filled with 26 L of 3.5% NaCl solution. Prior to electrochemical test, the solution was continuously aerated with air bubbles for 24 h to attain an oxygen saturation condition. The gas flow was maintained throughout the test, and the electrolyte was held at room temperature.

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