Corrosion Science 53 (2011) 208–216

Contents lists available at ScienceDirect

Corrosion Science

journal homepage: www.elsevier.com/locate/corsci

Electrochemical techniques for determining corrosion rate of rusted steel in seawater

Y. Zou [a], J. Wang [a,b,*], Y.Y. Zheng [a]

[a] Ocean University of China, Qingdao 266100, China
[b] State Key Laboratory for Corrosion and Protection of Metals, Shenyang 110015, China

ARTICLE INFO

Article history:
Received 4 April 2010
Accepted 4 September 2010
Available online 16 September 2010

Keywords:
A. Mild steel
B. Weight loss
B. IR spectroscopy
C. Rust
C. Oxygen reduction

ABSTRACT

Corrosion rates of mild steel for long-term immersion were estimated by electrochemical and weight-loss methods. The results showed that application of electrochemical methods yielded erroneous values. The main reason was that, β-FeOOH, produced after long-term immersion with high electrochemical activity in the inner rust layer, exerted significant influence. In electrochemical tests, even small polarization can make β-FeOOH participate in cathodic reaction, which leads to overestimating corrosion rate. In order to confirm it, electrochemical behaviour was studied in aerated and deaerated conditions to investigate the effect of rust layers on reduction reaction. After calibration, the electrochemical measurement result was coincided with the weight loss.

1. Introduction

Mild steel is the major material used for infrastructures in marine environments. It predominates in structural steel applications including ship hulls, offshore platforms, sheet piling and coastal facilities. Its general or uniform corrosion is the most important form of corrosion and is of considerable economic importance. World-wide there is increasing attention being given to reliable methods for measuring corrosion rate. Weight-loss measurement is currently the most direct and reliable method but time consuming and information limited. Electrochemical measurement, which tests faster with more information, and can be used in field detection combined with other methods, is a non-destructive, quantitative technique and a powerful tool for researching corrosion process.

But there are difficulties in studying corrosion behaviour of complex system such as rust/metal system by electrochemical measurement because the existence of rust complicates the electrochemical corrosion process. Electrochemical reactions under rust are not any more simple reactions including metal anodic dissolution and oxygen cathodic reduction but complex corrosion process composed of multiple sub-processes involving rust redox reactions, mass transportation though rust, electric charges movement between interfaces, microorganism propagation in porous rust and some other complex corrosion processes [1–3], which make metrical corrosion rates different between electrochemical and weight-loss measurements [4].

Electrochemical reactions are obviously consistent with the compositions of the rust layers and the compositions are not the same in different environments. The phase compositions of the corrosion products in an aqueous medium depend on different parameters, such as temperature, pH and the oxygen content. The presence of various ions in aqueous solution may also affect the phase compositions of the corrosion products. Refait [5] analyzed the rust layers formed on steel piles immersed during 25 years in the Bay of Brest, at Sainte Anne du Portzic by Raman spectroscopy and scanning electron microscopy. He found the rust layers consisted of three main strata, the inner one mainly composed of magnetite, the intermediate one of iron (III) oxyhydroxides and the outer one of hydroxysulphate green rust GR (SO_4^{2-}). Nishimura et al. [6] investigated the effect of chloride ion on the transformation of rust formed on the mild steel and observed that the content of β-FeOOH increased with the concentration of Cl ions in the environment. García et al. [7] used XRD and Mössbauer spectrometry to analyze the rust layers of weathering and mild steels exposed to a total immersion test. The rust layers obtained after 42 days of immersion could be classified into two types: on the basis of the compositions content, the outer one which fell down by hitting was composed of Fe_3O_4 > γ-FeOOH > β-FeOOH > α-FeOOH; the inner one which tightly bound to the steel surface was composed of Fe_3O_4 > β-FeOOH > γ-FeOOH > α-FeOOH.

Different compositions have different physical and chemical properties. In some cases, they can transform to others. Magnetite generally has been found at the metal/rust interface of thick rust

---

* Corresponding author at: Ocean University of China, Qingdao 266100, China. Tel./fax: +86 532 66781903.

E-mail address: jwang@ouc.edu.cn (J. Wang).

0010-938X/$ - see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.corsci.2010.09.011

layers [8,9]. According to Evans' model, the anodic oxidation of iron is balanced by the cathodic reduction of the first formed ferric rust to magnetite under wet conditions when access of oxygen is limited [10,11]. Continuous wetting can stabilize the magnetite phase [12]. The ferric oxyhydroxide of α-FeOOH is the final stable corrosion product, which is altered from γ-FeOOH, via amorphous substance, to final state after long-term exposure [13]. Musić et al. [14] proposed that the first step of the corrosion process of steel in a marine environment was the formation of $FeCl_3$, which further transformed to β-FeOOH by slow hydrolysis. Misawa et al. [15] reported that β-FeOOH could be obtained by the dry aerial oxidation of β-$Fe_2(OH)_3Cl$ which precipitated from slightly acidic solutions of ferrous chloride at room temperature.

Because some compositions such as β-FeOOH and γ-FeOOH are reducible, the corrosion process will change. Feliu et al. [16] reported that the presence or absence of dissolved oxygen in the saline medium had no influence on the response of rusted steel to the electrical signals applied since rust itself provided the cathodic reaction involved in the corrosion of the steel substrate. Hoffmann and Stratmann [17] considered that if the transport of oxygen was slow, the reduction of the oxide scale was possible when he studied the corrosion of rusted iron coated by organic lacquers. The redox of rust makes corrosion process more complex.

Since both the marine environment and rust/metal system were complex, researchers mostly studied metallic corrosion by estimating the material losses exposed in actual marine field for long term. Hudson and Stanners [18,19] reported data collected after 2 and 5 years of exposure. Forgeson et al. [20] reported data collected in the Panama Canal Zone for exposures to 16 years. Melchers [21–23] proposed a multi-phase phenomenological corrosion loss-time model to describe the marine corrosion behaviour for mild and low alloy steels. ASTM of US commissioned LaQue corrosion test centers to carry out field trials of various materials in 14 different actual marine fields of the world [24]. It provided a basis for evaluating the worldwide marine corrosion.

In addition to weight-loss measurement, some researches about rusted steel were also performed by electrochemical measurement. Feliu et al. [16,25] studied atmospherically rusted specimens with electrochemical impedance spectroscopy (EIS). The results showed that the shape in the impedance diagrams seemed to be markedly influenced by diffusion processes in the rust layer and/or by the porous nature of the rusted steel electrode. Since the majority of the Nyquist diagrams obtained with the rusted steel deviated from the typical semicircular form, it was not clear how kinetic information could be obtained from these diagrams. It therefore seemed preferable to use the d.c. data for the electrochemical determination of the corrosion rate for rusted steel [26]. But in investigation, they [27] also discovered that anomalously large differences between values of the polarization resistance (R_p) measured in the time and frequency domains posed a serious problem because the measurements were made under conditions far from the steady state. For this reason, selection of suitable scanning rate for d.c. test is significant.

In recent years, some researchers also observed that important deviation existed when estimating the corrosion rate of the rusted mild steel by electrochemical measurement because electrochemical signal could work on corrosion product [28,29]. Andrade et al. [30] confirmed that R_p measured in −0.7 V versus SCE were highly influenced by several redox processes that led to overestimation of the rebar corrosion rate by investing electrochemical behaviour of steel rebars with EIS. González et al. [4] proved that traditional polarization resistance method was not suitable for determining corrosion current density of rusted steel. The presence of 2-valent/3-valent iron in the rust could cause high pseudocapacitance values associated with redox reactions in the solid phase. The rust favoured corrosion both by providing a reducible material for the cathodic reaction and by acting as a porous electrode for the reduction of oxygen. Videm [31] showed that different electrochemical methods gave a large divergence in linear polarization (R_p) resistance when measuring corrosion rate for steel exposed to alkaline solutions by cyclic voltammetry, potentiostatic exposure, potentiostatic pulses, galvanostatic pulses and EIS. The dominating reason was that redox reactions of the corrosion product could consume a part of current, which decreased the polarization resistance and increased the corrosion rate.

In order to develop reliable detection and monitoring electrochemical techniques for researching long-term corrosion behaviour of rusted steel, this paper systematically studies the discrepancies between electrochemical and weight-loss results, analyzed the reasons and offered the calibration method.

2. Experimental

2.1. Materials preparation

Total immersion tests were performed on mild steel (Q235), coupons of dimensions 50 × 25 × 3 mm for weight-loss measurement with a hole for 5 mm in diameter located in the top middle and 10 mm in diameter embedded in epoxy resin for electrochemical measurement. The steel compositions are given in Table 1. The specimens were polished to 800 grit, cleaned ultrasonically in acetone and rinsed with distilled water. All the specimens were immersed synchronously in chest filled with seawater in laboratory conditions. Seawater for tests was from Huiquan Bay of Qingdao, filtrated before tests, static in the chest and replaced every week. The indoor average temperature was 20 °C. The test commenced on November 2007. The corrosion rates of coupons were measured periodically by weight-loss and electrochemical measurements. Triplicate recoveries were made every time for weight-loss measurement and averages were obtained.

The coupons immersed in seawater for different periods were taken out from the chest for weight-loss measurement. The rust layers were scraped off from the steel surface with keeping the steel substrate intact by a surgical blade, and residual rust on steel was removed by immersion in a mixed solution composed of 500 ml hydrochloric acid + 20 g hexamethylenetetramine + 1 L distilled water. After corrosion products had been completely removed, the specimens were rinsed with distilled water, dried with blower, and then weighed to determine their mass loss.

2.2. Analysis of composition and structure for rusted steel

Infrared spectra (IR) were obtained from a Nexus-380 infrared spectrophotometer with 32 scans in the ranges 400 and 1300 cm^{-1} with the accuracy of 4 cm^{-1}. The outer rust layers were scraped off using a coarse wire brush and inner layers by a surgical blade. The rust products were grounded into fine powder and pressed to pellets with appropriate amount of KBr. Cross-sections of the surface for corrosion products were observed by JT-2182IIcolor video camera.

2.3. Electrochemical measurements

Electrochemical measurement was implemented with a PARSTAT 2263 potentiostat/galvanostat electrochemical system

Table 1
Chemical compositions in wt.% of Q235 mild steel.

Chemical composition	C	Si	Mn	P	S
Mass%	0.18	0.30	0.32	0.040	0.040