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Atmospheric corrosion monitoring of a weathering steel under an electrolyte film in cyclic wet–dry condition



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1. Introduction

The atmospheric corrosion of steels usually proceeds under a thin liquid film on the steel surface [1,2]. The thickness of the liquid film alternately increases and decreases due to the daily cyclic change in humidity and temperature of the atmospheric environment [3,4]. This change in thickness can bring a number of effects to the atmospheric corrosion processes. For instance, the reduction rate of the dissolved oxygen is controlled by limited diffusion process in the case of thick liquid film but by charge transfer reaction for thin liquid film. Besides, the change in the electrolyte concentration and thickness can greatly influence its conductivity [5]. On the one hand, the thinning out of the liquid film during its evaporation process brings a decrease in the intersection area of the electrolyte enhancing its resistance. On the other hand, the evaporation process also concentrates to an increase in the salt concentration in the liquid film. Moreover, as the wet-dry cycle proceeds, the surface of steels can be rusted, and the formed rust layer greatly affects the corrosion behavior of the steel and the amount of water associated with the surface properties [6]. Firstly, the grown rust can change the diffusion track of the dissolved oxygen and resist the transportation of some anions to the underlying steel substrate [7]. Furthermore, FeOOH as one composition of the rust can be cathodically reduced to magnetite during the subsequent rusting process [8]. Therefore, the rust formation on the steel surface greatly influences the understanding in atmospheric corrosion mechanism and the accuracy of the film thickness measurements.

ABSTRACT

Electrochemical Impedance Spectroscopy (EIS) and film thickness measurements have been employed to study the corrosion monitoring of steel under an electrolyte film in wet–dry cycles simulating a coastal atmosphere. The results indicate that within each cycle, the corrosion rate increases during drying process due to an increase in CI^- concentration and an enhancement of oxygen diffusion by thinning out of the electrolyte. As corrosion process proceeds, the corrosion rate increases greatly and reaches a maximum. During subsequent corrosion stage, the corrosion rate decreases greatly and keeps at a low value due to the formation of a stable rust layer.

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In general, different metal has different critical thickness for its maximum atmospheric corrosion rate. Tomashov [9] reports that the atmospheric corrosion rates of metals show a maximum when the liquid film to be as thick as 1 μ m. Stratmann [10] monitors the corrosion rate of iron during drying and obtains a maximum corrosion rate at a thickness of approximately 10 µm. Nishikata et al. [11] finds that copper covered with an acidic solution layer containing sulfate ions shows a maximum corrosion rate at a thickness of 20–30 um. Fu et al. [12] reports that for O235 carbon steel the critical thickness is about 17 µm. These studies promote better understanding of the atmospheric corrosion of metals with a thin liquid film covering. However, these investigations are carried out on metal substrate without rust layer covering. In practice, steels often have different rust layers, and therefore it should be of great importance to investigate the corrosion evolution of steel submitted to continuous wet-dry cycles under different rust layers, which is vital for understanding the corrosion evolution mechanism of steel under an electrolyte film in cyclic wet-dry condition.

EIS has been proven to be a useful technique for monitoring atmospheric corrosion of steel [13]. Nishikata et al. [14] applied EIS to elucidate the effects of the thickness and the pH of the electrolyte films on the initial atmospheric corrosion stage of iron. Li et al. [15] used chip-shaped bi-electrodes to study the evolution of EIS of carbon steel in one wet–dry process. Fu et al. [12] utilized a chip-shaped multi-electrodes to monitor the corrosion of mild steel under an alternate wet–dry condition at a very low humidity. However, less work has been done to investigate the corrosion evolution of weathering steel under an electrolyte film, especially when the steel was covered with a thick rust layer.





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In the present work, EIS and thickness measurements have been employed to study the corrosion monitoring of a weathering steel under a thin liquid film submitted to wet–dry cycles in a simulated coastal atmosphere maintained at 30 °C and 60% RH (relative humidity). One aim of the investigation is to study the effect of electrolyte thickness on the corrosion evolution of steel in each wet–dry cycle, and the other one is to gain information on the corrosion kinetics as a function of cyclic wet–dry cycle. Besides, the corrosion evolution mechanism has been discussed.

2. Experimental

2.1. Electrode preparation

In this study, a weathering steel was used as the electrode material and its composition was (in mass%): 0.06 C, 0.0135 Si, 1.16 Mn, 0.38 Cr, 0.16 Ni, 0.24 Cu, 0.019 P, 0.005 S and Fe. The steel was sectioned into a pair of comb-like electrodes as shown in Fig. 1(a). Then, the two electrodes were embedded in epoxy resin with the comb fingers crossing but not contacting each other as schematically shown in Fig. 1(b) [5,12], and the surface area of the two-electrode was approximated 1 cm². Fig. 1(c) shows the top view and transverse cross-sectional view of the embedded sample. After being ground on SiC paper to 1000 grit, the two-electrode cell was stored in a desiccator for 24 h and then subjected to the wet–dry cyclic corrosion tests (CCT). During EIS measurement, one electrode worked as working electrode, and the other one worked as reference electrode and auxiliary electrode as indicated in Fig. 1(d).

2.2. Wet-dry cyclic corrosion tests

A self-made chamber with temperature and relative humidity (RH) control units was used for the tests. The simulated environmental condition in the chamber was maintained at 30 ± 1 °C and $60 \pm 2\%$ RH by using the humidity control system containing

water-glycerol mixture, the ratio of which was prepared according to ASTM D 5032 [16]. After the electrodes cell being placed in the chamber, the CCT was then performed. The first CCT was conducted by wetting the electrode surface with 0.05 mol L^{-1} NaCl solution (simulating a coastal environment [9]) with an approximate volume of 50 μ L cm⁻², and drying the electrode in the chamber for 12 h. For other CCT cycles, the same working steps as the first CCT were repeated, but a same volume of distilled water was used as a solution instead of NaCl solution for keeping the amount of chloride ions a constant during the whole test. One CCT refers to the period that from wetting the surface with electrolyte to its drying, and then enters the subsequent CCT cycle. Clearly, at the beginning of the first CCT, NaCl solution was added on the surface, however, from the second CCT, distilled water of same volume was added to the surface. The whole exposure experiment of the cell was performed for 60 CCT numbers.

2.3. Electrolyte thickness and EIS measurements

During the whole test, the electrode cell has been placed on an analytic balance BS 224 S, Satorius with accuracy d = 0.1 mg, and its USB interface is connected with a computer for recording the data of the weight change. When the electrolyte is laid on the surface of the cell, the observed weight of the electrolyte is read and recorded in the computer.

The weight of the electrolyte film (W_e) is obtained as follows:

$$W_e = W_s - W_d \tag{1}$$

where W_s stands for the observed weight of the cell during the evaporation process; W_d is the initial weight of the cell for the first CCT, and is the weight of the dried rusted-cell when a new CCT cycle starts. The thickness of electrolyte film (*X*) can be monitored by Eq. (2):

$$X = \frac{W_e}{\rho S} \tag{2}$$



Fig. 1. Schematic diagram in illustrating the arrangement of the two-electrode cell used for EIS measurement. (a) Top view of the comb-like electrode. (b) Top view of the comb-like electrodes with their fingers crossing with each other with touching. (c) Top view and transverse cross-sectional view of the embedded electrodes. (d) Enlarged transverse cross-sectional view in illustrating functions of the two electrodes.

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