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Short Communication

Influence of Lepidocrocite Film Formed in-situ on Corrosion Behavior of Weathering Steel in the Solution without Cl^-

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The corrosion behavior of lepidocrocite (γ-FeOOH) films in-situ prepared on the surface of Cor-TenA weathering steel (WS) has been investigated by means of electrochemical techniques in 0.25mol/L Na_2SO_4 solution. The results show slightly protective ability for the γ-FeOOH film grown in-situ to the substrate because of the γ-FeOOH film changing to compact as the corrosion reaction progresses. But, at the initial stages of the reaction, the films participated in the cathodic reaction and provided no protection to the substrate.

Keywords: Atmospheric corrosion; Lepidocrocite film; Electrochemistry

1. INTRODUCTION

When the metal materials were prolonged exposed, the materials would be corroded in all kinds of environments, with formation of corrosion product films on the exposed surfaces. The corrosion product films, with different composition, micro-structure, and thickness, strongly influence the corrosion behavior of structure materials. Studies have shown that variations in the composition of corrosion products on carbon steel with prolonged exposure time often lead to considerable variations in corrosion behavior. Among the various corrosion products, γ-FeOOH and α-FeOOH has been shown to play key roles in the corrosion process [1-4]. Leidheiser et al. [4] reported formation of γ-FeOOH at the early stages of corrosion and later transformed into a mixture of α-FeOOH and γ-Fe_2O_3, with better protective ability. T. Kamimura et al. [5,6] pointed out that the mass ratio “α/γ” of crystalline α-FeOOH to γ-FeOOH, in the rust film could characterize its protective ability. Larger α/γ corresponds to higher corrosion resistance. Accordingly, several studies[5-8] attribute the protective ability of rust film to α-FeOOH. On the other hand, the contributions of the pure γ-FeOOH and other components in the corrosion product film to the protective ability have not received much attention at present.

In fact, the protective ability of the corrosion product films formed on materials in natural environments results from a cooperative effect involving the different oxides, even though each oxide has its own specific physical and chemical characteristics. To clarify the key factors determining the protective ability of corrosion product films, it is necessary to clarify the corrosion behavior of the oxides individually.

Since γ-FeOOH is one of the mainly corrosion products on the surface of structural steels, Cor-TenA weathering steel (WS) was selected as the test specimen and pure γ-FeOOH film was fabricated in-situ on the surface by chemical methods. The electrochemical characteristics and protective abilities of the pure rust film were studied by electrochemical techniques.

2. EXPERIMENTAL

2.1. γ-FeOOH film preparation in-situ

The material used in this study was Cor-TenA WS. The cast alloy samples (15×10×2mm) was ground with 1000 grit SiC paper, cleaned in distilled water and anhydrous alcohol, and dried with cool air. The reaction temperature was controlled at 30±1^{o}C in a water bath. 1.0 ml of 10% H_2SO_4 solution was dropped on the surface of the Q235 to form the $FeSO_4$ liquid film and left for about 30 mins. Subsequently 0.5ml of 3.75×10^{-5} mol/L EDTA solution was dropped into the liquid film and was left for about 10 mins. After this, 1ml of NH_3H_2O solution (pH = 8.7) was dropped on the surface and the liquid film was oxidized by bubbling O_2. The NH_3H_2O solution was continuously replenished on the surface until a yellow film was formed in-situ, which is the γ-FeOOH rust film.

2.2. Samples characterization

The morphology of the rust films was analyzed by scanning electron microscopy (SEM, Philips XL30). The rust film constituents were identified using X-ray diffraction (XRD, Pananlytital). The polarization and electrochemical impedance spectroscopy (EIS) were carried out using a PARSTAT 2273 Electrochemical Measurement System manufactured by PRINCETON Applied Research Inc. The potentiodynamic polarization measurements were carried out at a sweep rate of 0.33mV/s. Anodic and cathodic polarization measurements were taken for the different specimens. EIS measurements were carried out over the frequency range 100kHz to 10mHz with a 5mV amplitude signal perturbation at the open circuit potential (OCP). Potentiostatic polarization experiments were performed at -850 mV to measure the variation of current with time in order to obtain information on the reversion of the rust film.

2.3 Three-electrode cell test

Test samples were connected to a Cu leading wire, wrapped with polytetrafluoroethylene tape and coated with a mixture of paraffin-resin leaving an exposed working area 1 cm^2.

All electrochemical measurements were performed in a conventional three-electrode cell, using a large platinum plate as the counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The test solution was 0.25mol/L Na_2SO_4. A water bath was used to keep the solutions at 30±1 ^oC during testing.

3. RESULTS AND DISCUSSION

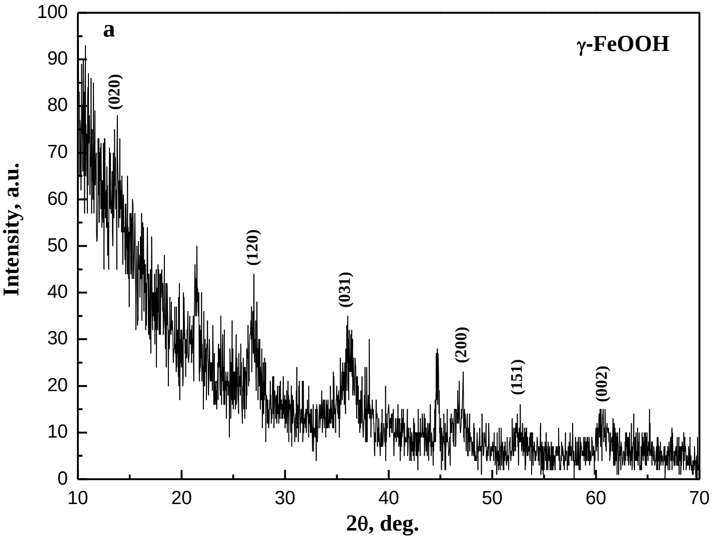

Figure 1. XRD of the rust film

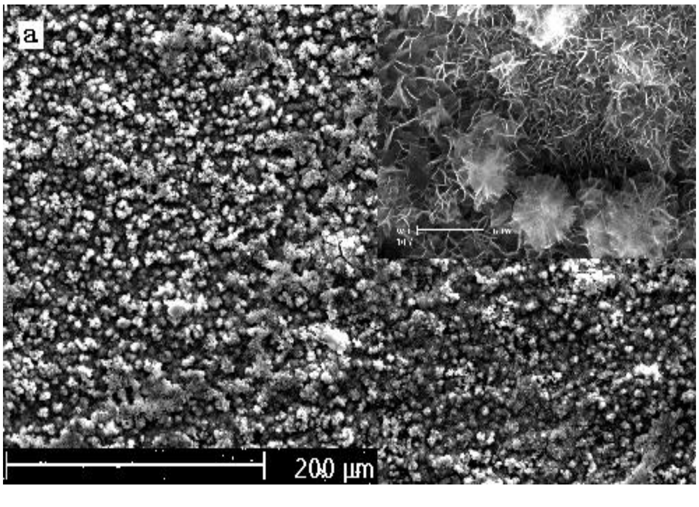

Figure 2. SEM images of the rust film.

XRD plots for the rust films prepared in-situ were given in Fig. 1, show that the fundamental structure and composition of the rust films are γ-FeOOH(JCPDS,80098#). The surface morphologies of the films were observed and the SEM image is shown in Fig.2. Fig.2 depicts a needle-like shaped film formed on the sample, which is similar to typical γ-FeOOH[9].

The polarization and impedance characteristics of Cor-TenA WS with and without γ-FeOOH film were performed in 0.25mol/L Na_2SO_4 solution.

Being the reduction of γ-FeOOH during the cathodic polarization reactions, the anodic and the cathodic polarization curves were measured separately from the OCP to anode or cathode, and shown in Fig. 3.

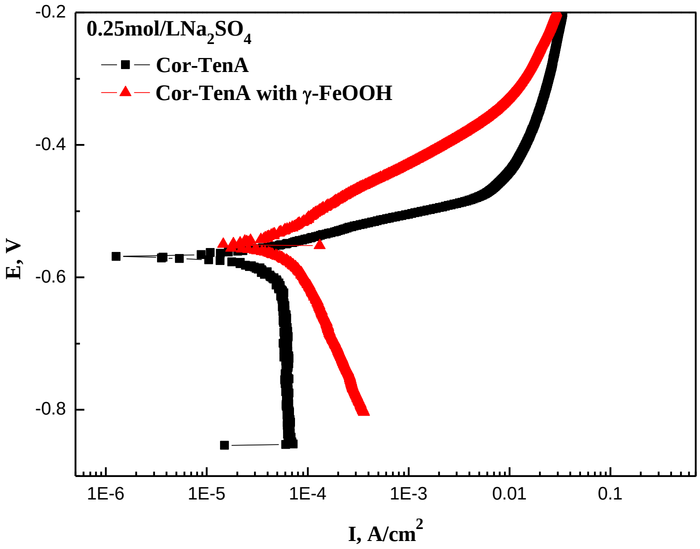

Figure 3. Potentiodynamic polarization plots of cast Cor-TenA and Cor-TenA with γ-FeOOH film in 0.25mol/LNa_2SO_4 solution

The polarization curves show that the γ-FeOOH film did not notably influence the anodic polarization behavior of Cor-TenA WS in 0.25mol/LNa_2SO_4 solution at potentials > -0.4V. Nevertheless, the anodic current on the samples with the γ-FeOOH film was reduced, which suggests that the rust film restricted access of the corrosion media and inhibited the process of the anodic reaction.

In the cathodic domain, the polarization curves for Cor-TenA WS with and without γ-FeOOH film are markedly different and the data clearly shows that the rust film accelerated the kinetics of the cathodic process. The cathodic reaction was diffusion controlled to cast Cor-TenA WS, however, the electrochemical process controlled the reactions for Cor-TenA WS with γ-FeOOH film and the cathodic current increased greatly.

The protective ability of γ-FeOOH film to the Cor-TenA WS would be further characterized from impedance measurements shown in Fig.4.

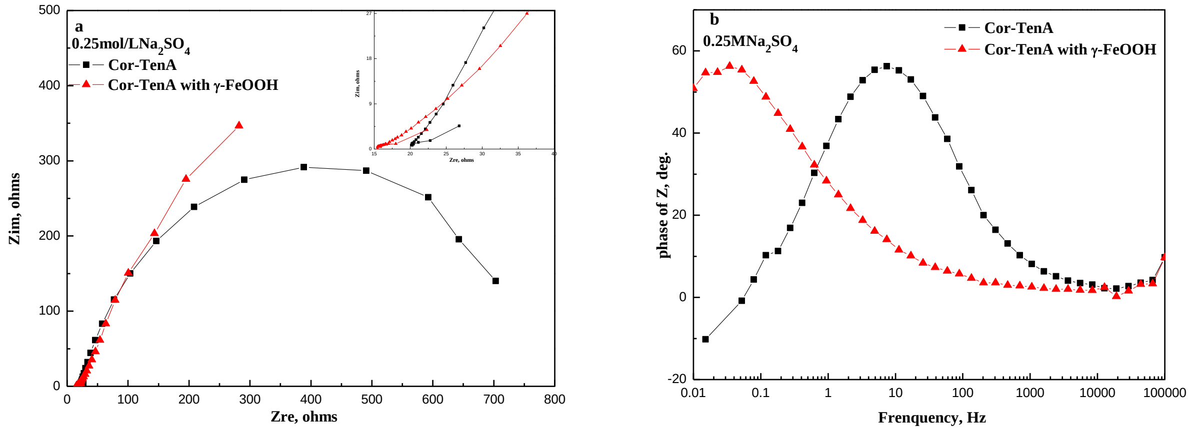

Figure 4. Nyquist (a) and Bode plots (b) of the cast Cor-TenA and Cor-TenA with γ-FeOOH film in 0.25mol/LNa_2SO_4 solution

The The Nyquist and Bode plots (in Fig.4) of the cast Cor-TenA WS reflect only one capacitive loop within the studied frequency range, which suggests that the electrode reaction was potential controlled. For Cor-TenA with γ-FeOOH, the Nyquist plots consist of two semi-circles (in Fig.4(a)), and the Bode plots displayed two time constant (in Fig.4(b)). It has been suggested [10, 11] that Nyquist diagrams consist of two semi-circles: one at high frequencies due to the covering, the other at low frequencies due to a process of diffusion between the electrolyte and the layer. The equivalent circuits (Fig.5(a and b)) were used to model the impedance response of the electrode/electrolyte interface. The values of solution resistance (R_s), charge-transfer resistance (R_t), and total capacitance (Q) of the constant phase element (CPE) were calculated by simulating the experimental data with ZSimpWin software. The results are listed in Table 1.

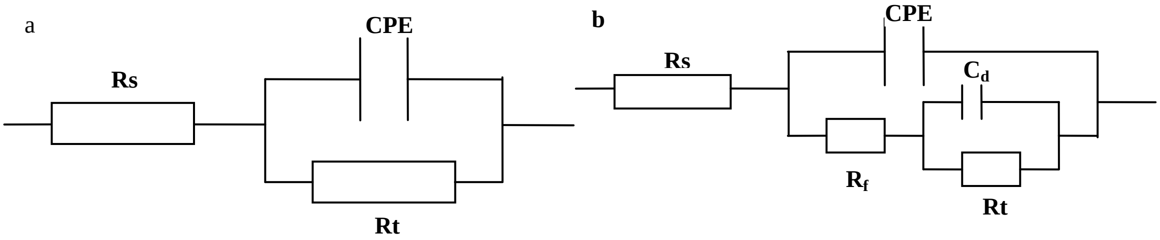

Figure 5. Equivalent circuits modelling the electrode of Cor-TenA(a) and Cor-TenA with γ-FeOOH film(b)

The values of R_t are strongly dependent on the rust film characteristics and describe the corrosion resistance of the metal materials. According to the equivalent circuit parameters of EIS results, the R_t value for the γ-FeOOH film is bigger than that of the cast Cor-TenA WS, which means that γ-FeOOH film improved the corrosion resistance of Cor-TenA WS, and reduced the corrosion reaction.

Table 1. Equivalent circuit parameters of EIS results.

Sample(0.25MNa_2SO_4)	**R_s, ohm cm^2**	**R_{rust}, ohm cm^2**	**C, μF /cm^2**	**n**	**R_t , ohm cm^2**	**CPE, μF/cm^2**	**n**
Cor-TenA	18.24	——	——	——	1587	0.0002567	0.8398
with γ- FeOOH	16.01	21.25	0.007136	0.6749	2071	0.009794	0.7844

4. CONCLUSIONS

Pure γ-FeOOH film had been prepared in-situ on Cor-TenA WS. The γ-FeOOH film shows similar cathodic electrochemical behavior, but its influence on the corrosion behaviors of the substrate is quite distinct. The cathodic corrosion process of Cor-TenA WS with γ-FeOOH is electrochemical controlled. At the initial stages of the reaction, the films participated in the cathodic reaction and provided no protection to the substrate, but as the corrosion reaction progresses, the γ-FeOOH film changes to compact, thus improving the film protectiveness.

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