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Evolution of corrosion of MnCuP weathering steel submitted to wet/dry cyclic tests in a simulated coastal atmosphere

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ABSTRACT

The evolution of rust on MnCuP weathering steel submitted to a simulated coastal atmosphere was investigated by corrosion weight gain, scanning electron microscopy, X-ray diffraction, and electrochemical methods. The results indicate that the higher corrosion rate during the first stage than that during the second stage is related closely to the rust composition and electrochemical properties. The corrosion rate evolution is caused by the formation of a protective rust layer with a higher relative amount of α-FeOOH. The rust initially enhances and then stabilizes the cathodic process, but the anodic process tends to be inhibited by the protective rust layer.

1. Introduction

It is widely accepted that the wet/dry cyclic process of the steel surface is mainly responsible for the atmospheric corrosion of steel [1–3], which is usually an electrochemical process under thin aqueous film. Generally, higher atmospheric temperature and prolonged wetness lead to a higher rusting rate of the steel, as the corrosion reactions can take place at a faster rate under the conditions, especially with the presence of salt contaminations [4,5]. Chloride ion is one of the most significant natural contaminants in coastal atmospheric environments. With the presence of a lower chloride concentration, it only plays a key role during the initial atmospheric corrosion stage; as the rust layer grows in thickness, the supply of fresh chloride ions may gradually diminish and as a result, the formation of chlorides will be slower [6]. It is reported that the rust layer on weathering steel in low chloride ion atmosphere is of cation selectivity, and thus the rust layer is protective [7–9]. But, with the presence of a higher chloride concentration, it has a deleterious effect to the corrosion kinetics, rust composition and structures. The β-FeOOH exists and can work as a reservoir of chloride ions [10], and then the rust layer itself would become porous and can facilitate the transportation of chloride ions from outside easily, which promotes the further corrosion [11]. Li et al. [12,13] reported that the rust layer on weathering steel in Qinghai salt lake atmosphere with higher content of chloride ions is non-protective. In past decades, researches [14–18] on atmospheric corrosion of steels in chlorides containing environments are mainly focused on the effect of chloride ion concentrations on the corrosion behaviour of steels with different alloy elements. In fact, weathering steels often have different rust layers [19], and the rust layers formed during different corrosion stages may have different composition and structures that can lead to distinct corrosion behaviour of the steel. Thus, it should be of great importance to gain information about the corrosion evolution and the rust layer properties, which is vital for predicting the long-term corrosion process of steel structures.

MnCuP steel is a kind of low cost weathering steel, not alloyed with Cr and Ni elements [20], and it shows higher resistance to atmospheric corrosion not only in simulated coastal atmosphere but also in simulated industrial atmosphere and coastal–industrial atmosphere containing chlorides and sulphur dioxide [20]. To investigate the effect of chloride on the atmospheric corrosion evolution of the steel, a coastal atmosphere based on the chloride concentration in the atmosphere of Wanning city, China was simulated. The wet/dry cyclic corrosion test (CCT) can simulate atmospheric corrosion under controlled relative humidity (RH) and temperature, and it is one of the most popular simulated atmospheric corrosion tests [19]. In the present study, CCT was employed to investigate the corrosion evolution of MnCuP weathering steel in the simulated coastal atmosphere, paying particular attention to the corrosion

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kinetics, and evolutions in the rust morphology, composition and structures, and electrochemical characteristics.

2. Experimental

2.1. Wet/dry cyclic corrosion test

The sample material is MnCuP weathering steel that contains (in mass%) 0.196 C, 0.49 Si, 1.89 Mn, 0.046 P, 0.013 S, 0.292 Cu and Fe. The samples were ground with SiC paper down to 600 grade emery paper. After being cleaned with ethanol, the samples were stored in a desiccator for 24 h, and then subjected to the wet/dry cyclic corrosion test (CCT) [21,22]. One CCT consists of (I) weighing the initial sample; (II) wetting the sample surface with 40 μL cm^{-2} of 0.05 mol L^{-1} NaCl solution (simulating the coastal atmosphere based on the chloride concentration in the atmosphere of Wanning city, China [23]); (III) drying the sample in a chamber maintained at 30 °C and 60% RH (relative humidity) for 12 h; (IV) re-weighing the sample after drying; (V) rinsing the sample with distilled water to prevent the accumulation of progressive salt and drying the sample before application of fresh corrosion electrolyte; (VI) repeating the preceding steps from (II) to (V) for different CCT numbers. One N (CCT number) equals to a half day.

2.2. Rust analysis

The powdered rust was scraped off from the rusted samples using a razor blade and then the powdered rust sample was characterised by means of X-ray diffraction (XRD) to determine its composition. To compare the differences of the intensity for different samples, the amount of rust for each analysis was kept the same. So, in this case, the intensity of certain phase such as α-FeOOH, β-FeOOH, γ-FeOOH and Fe_3O_4, can reflect its relative amount [24]. The rusted samples for cross-sectional analysis were observed using scanning electron microscopy (SEM).

2.3. Electrochemical measurements

Polarisation curves and electrochemical impedance spectroscopy (EIS) measurements were carried out using a classical three electrodes cell with platinum as counter electrode, saturated calomel electrode (SCE) as reference electrode, and the naked or rusted steel samples with an exposed area of 1 cm^2 as working electrode. The polarisation curves were obtained at a 10 mV min^{-1} constant scan rate. The frequency range for EIS was from 100 kHz to 10 mHz with a 5 mV amplitude signal at open circuit potential. The corrosive electrolyte was 0.05 mol L^{-1} NaCl solution. All the measurements were carried out at room temperature (25 °C).

3. Results and discussion

3.1. Corrosion kinetics

Fig. 1 shows the corrosion kinetics of MnCuP weathering steel in the simulated coastal atmosphere as a function of the CCT number. Fig. 1(a) shows that the corrosion weight gain of the steel increases gradually with increasing the CCT number. Fig. 1(b) reproduces the results in Fig. 1(a) by plotting the weight gain against the CCT number in log–log coordinates. Clearly, the whole corrosion process of the steel can be divided into two corrosion stages: a higher slope for the first corrosion stage and a lower slope for the second corrosion stage, and the transition point is at approximately 20 CCT. The weight gain results in the two corrosion stages can be fitted, respectively by Eq. (1) [1,3,8,11]:

$$\log \Delta W = \log A + n \log N \tag{1}$$

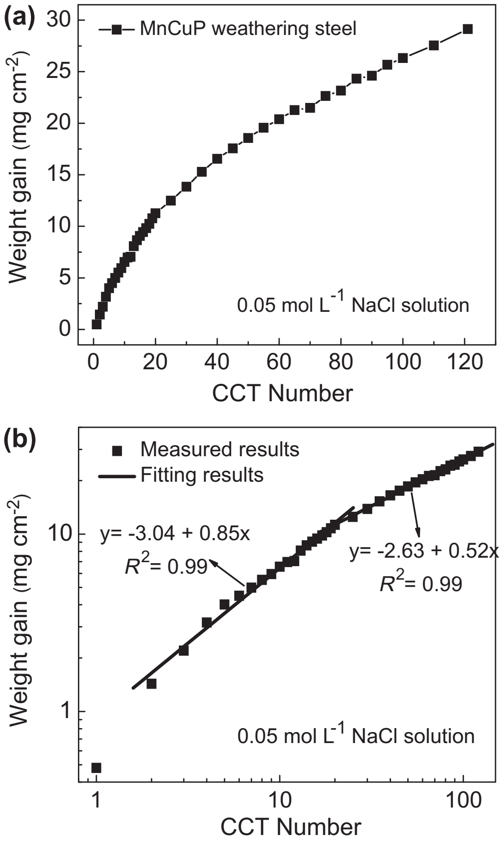

Fig. 1. Corrosion weight gain results of MnCuP weathering steel in simulated coastal atmosphere as a function of the CCT number. (a) Linear plot; and (b) bilogarithmic plot.

where ΔW is weight gain (mg cm^{-2}), N is the CCT number (corrosion time), and A and n are constants. The linear fitting has been done by the OriginPro 7.5 software, and the obtained equations are as follows:

For the first corrosion stage,

$$\log \Delta W = -3.04 + 0.85 \log N \quad N \leqslant 20 \tag{2}$$

For the second corrosion stage,

$$\log \Delta W = -2.63 + 0.52 \log N \quad N > 20 \tag{3}$$

Based on Eqs. (2) and (3), Fig. 2 shows that corrosion rate (mg cm^{-2} d) of MnCuP steel during the whole process as a function of the CCT number [20]. The corrosion of MnCuP weathering steel

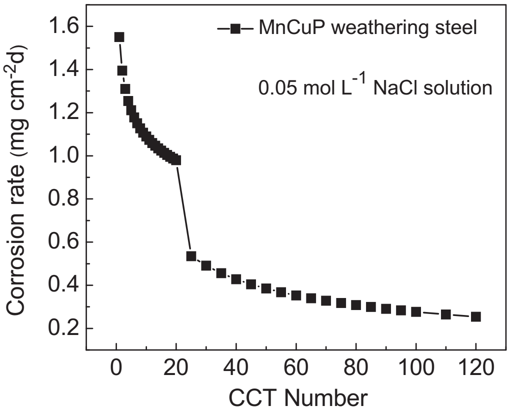

Fig. 2. Corrosion rate of MnCuP weathering steel in simulated coastal atmosphere as a function of the CCT number.