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Effect of sulphur dioxide on the corrosion of a low alloy steel in simulated coastal industrial atmosphere

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ABSTRACT

This investigation aims to study the effect of SO_2 on the corrosion of a low alloy steel in simulated coastal industrial atmospheres. The results indicate that the corrosion weight gain of the steel firstly increases with increasing SO_2 content to a certain level and then decreases with further increasing the SO_2 content. Besides, higher SO_2 content promotes the formation of α-FeOOH and inhibits the formation of γ-FeOOH. Moreover, it seems that the deterioration effect of SO_2 to steel corrosion is not obvious in the initial corrosion stage and SO_2 begins to accelerate the steel corrosion as the corrosion process increases.

1. Introduction

Chlorides and sulphur dioxide (SO_2) are the two dominant constituents influencing the corrosion rates of steels under outdoor exposures conditions in addition to the surrounding humidity and temperature. Accordingly, coastal atmosphere containing chlorides and industrial atmosphere containing SO_2 have been classified as the two atmospheric corrosion environments of steels [1–3]. In coastal atmosphere, chloride ion can penetrate the rust layer and directly attack the steel substrate and this is the main anodic process; the cathodic corrosion process includes the reductions of dissolved oxygen and FeOOH [4,5]. In industrial atmosphere, iron can be corroded into $FeSO_4$ involving SO_2 and O_2, and $FeSO_4$ can be oxidised to rust, freeing SO_4^{2-}, which acidifies, then corrodes more iron, giving fresh $FeSO_4$, hence more SO_4^{2-}, and so on [6–8]. This cyclic process can produce H_2SO_4 and thus accelerate the rusting process. The cathodic corrosion process includes the reduction of H^+ in the industrial atmosphere [9]. In addition, the rust in coastal atmosphere contains β-FeOOH, which does not exist in the rusted steel samples in industrial atmosphere [10].

Coastal atmosphere and industrial atmosphere are the two environments that have been received much attention during the past decades in the research field of atmospheric corrosion. However, the atmosphere in many cities along the coastal lines such as in China and other developing countries has been polluted with SO_2 due to the development of industry, and there the atmosphere has been changed to coastal industrial atmosphere [11–14]. Liang et al. [15] carried out sixteen-year atmospheric corrosion exposure study of steels, and found that SO_2 only has obvious deterioration effect in the initial corrosion exposure of steels. However, Allam et al. [16] investigated the atmospheric corrosion of steel in the Arabian Gulf, and indicated that chloride ions are more aggressive than sulphate ions during the initial atmospheric corrosion stage of steels. Therefore, the effect of SO_2 on the corrosion behaviour of steel in atmosphere containing Cl^- is not clear, and the corrosion of steel in coastal industrial atmosphere has not been systematically studied. Besides, different SO_2 content in the atmosphere may lead to different corrosion behaviour of steel in coastal industrial atmosphere, and the effect of SO_2 content on the corrosion behaviour of steel is also not quantified. In addition, almost all the atmospheric corrosion data of steels were obtained by field exposure test [17,18], which can really reflect the actual corrosion behaviour of steel in certain atmospheric environment but cannot reflect the dependence of SO_2 or Cl^- on the atmospheric corrosion of steels due to the difficulties in controlling the field conditions [19–21].

Wet/dry cyclic corrosion test (CCT) based on saltwater spray and followed by drying can simulate atmospheric corrosion under controlled relative humidity (RH) and temperature [22–24], and thus can provide accurate information in determining the effect of SO_2 on the atmospheric corrosion of steel in coastal industrial atmospheres. The present investigation aims to study the effect of SO_2 on the corrosion of a low alloy steel submitted to CCT in

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simulated coastal industrial atmospheres, and the corrosion mechanism has also been discussed.

2. Experimental

2.1. Wet/dry cyclic corrosion test

A low alloy steel was used in this investigation and its composition was listed in Table 1. The steel was cut into coupons with size of 50 mm × 50 mm × 5 mm for the wet/dry cyclic corrosion tests and 10 mm × 10 mm × 5 mm for electrochemical measurements. Then the samples were encapsulated in epoxy resin mounted inside a PVC pipe, and ground with SiC paper down to 600#. After being cleaned with ethanol, the samples were stored in a desiccator for two days, and then subjected to the wet/dry cyclic corrosion test (CCT) [22]. It consists of (1) weighing the initial sample; (2) wetting the sample surface with electrolyte of 40 μL cm^{-2}; (3) drying the sample in a chamber maintained at 30 °C and 60% RH for 12 h; (4) re-weighing the sample after drying; (5) rinsing the sample with distilled water to prevent the accumulation of progressive salt followed by drying the sample before application of fresh corrosion electrolyte; (6) repeating the above steps from (2) to (5) for different CCT cycles. In the following, *N* is the number of CCT cycles, and one CCT equals to 12 h. According to ISO 9223 [25], Table 2 summarises the NaCl electrolytes containing different Na_2SO_3 content for simulating coastal industrial atmospheres.

2.2. Synchrotron radiation XRD analysis

The scraped rust layer was ground to fine powders in a mortar with a pestle and then characterised by XRD technique to determine the rust phases. The X-ray diffraction data were obtained at beamline BL14B1 of the Shanghai Synchrotron Radiation Facility (SSRF) at a wavelength of 1.2398 Å. BL14B1 is a beamline based on bending magnet and a Si(1 1 1) double crystal monochromator was employed to monochromatize the beam. The size of the focus spot is about 0.5 mm and the end station is equipped with a Huber 5021 diffractometer. NaI scintillation detector was used for data collection. The special advantage provided by synchrotron radiation is that it permits XRD measurements with increased energy, spatial and time resolution. Compared to the conventional X-ray tubes, the synchrotron radiation is of times brighter and faster counting statistics on similarly sized samples. The high intensity of synchrotron X-ray beams greatly improves the signal-to-noise ratio, allowing the analysis of minor amounts of material [26]. To compare the differences of the intensity for different XRD samples, the amount of rust for each analysis was kept the same. Therefore, in this case, the intensity of certain phase such as α-FeOOH, γ-FeOOH and Fe_3O_4 can semi-quantitatively reflect its relative content [27].

Table 1
Chemical compositions of the low alloy steel studied (in mass%).

Element	C	Si	Mn	S	P	Cr	Ni	Cu	Fe
Content	0.06	0.014	1.16	0.005	0.019	0.38	0.16	0.24	Bal.

2.3. Electrochemical measurements

The polarisation curves and electrochemical impedance spectroscopy (EIS) measurements were carried out using a classical three electrodes cell with platinum as the counter electrode, saturated calomel electrode (SCE) as the reference electrode, and the rusted steel samples with an exposed area of 1 cm^2 as the working electrode. The polarisation curves were obtained using M273A electrochemical workstation at a constant scan rate of 10 mV min^{-1}, and i_{corr} was obtained by the linear fitting from potential range of −10 mV to +10 mV versus open circuit potential. The frequency range for EIS was from 100 kHz to 10 mHz with an amplitude of 10 mV (rms) at open circuit potential. The working electrolytes were the coastal industrial atmospheres simulating electrolytes. All the measurements were carried out at room temperature (25 °C ± 1 °C).

3. Results and discussion

3.1. Corrosion kinetics

Fig. 1 shows that the corrosion weight gain of the low alloy steel gradually increases with increasing the wet/dry CCT number in the

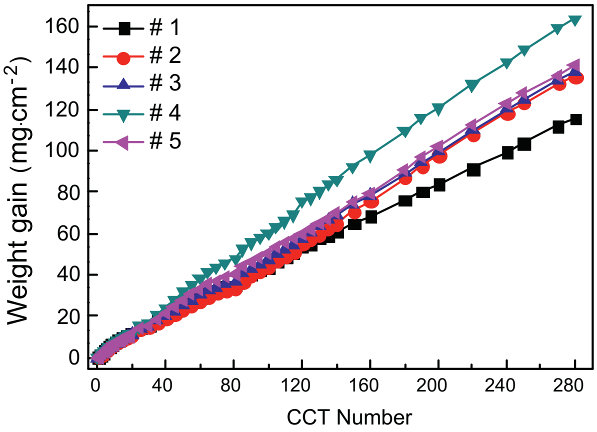

Fig. 1. Corrosion weight gain result of the low alloy steel with prolonged CCT number in simulated coastal industrial atmospheres with different SO_2 content. The electrolytes for simulating coastal industrial atmosphere with different SO_2 content were prepared by adding different amount of Na_2SO_3 into 0.05 mol/L NaCl solution. The Na_2SO_3 content was set to be 1, 1.67, 2.5, 5, and 10 mmol/L, respectively.

Table 2
The electrolytes characteristics and corrosivity for simulating the coastal industrial atmosphere with different SO_2 content. The electrolytes were prepared by adding different amount of Na_2SO_3 into NaCl solutions.

Atmosphere	pH	NaCl			Na_2SO_3		
		Concentration (mol/L)	Deposition rate (mg/m^2 d)	ISO [25], corrosivity category	Concentration (mmol/L)	Deposition rate (mg/m^2 d)	ISO [25], corrosivity category
#1	4.0	0.05	710	S_3	1	25.6	P_1
#2	4.0	0.05	710	S_3	1.67	42.752	P_2
#3	4.0	0.05	710	S_3	2.5	64	P_3
#4	4.0	0.05	710	S_3	5	128	P_3
#5	4.0	0.05	710	S_3	10	256	$>P_3$