ELSEVIER

International Journal of Minerals, Metallurgy and Materials
Volume 16, Number 1, February 2009, Page 58

Materials

Corrosion behavior and corrosion products of a low-alloy weathering steel in Qingdao and Wanning

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(Received 2008-03-09)

Abstract: A newly developed low-alloy weathering steel has been exposed in two coastal sites (Qingdao in the north, Wanning in the south) in China for one year. The samples in Wanning corroded far more seriously than those in Qingdao. The rust layer formed on the steel was analyzed by X-ray diffraction (XRD), scanning electron microscopy (SEM), N_2 adsorption approach, polarization curves, and electrochemical impedance spectroscopy (EIS). The rust formed in Qingdao contains more X-ray amorphous compounds and is more compact than that formed in Wanning. Cr and Cu are enriched in the rust layer near the steel matrix, and the phenomenon is more obvious in Qingdao than in Wanning. The rust layer formed in Qingdao suppresses the anodic and cathodic reaction more remarkably than that formed in Wanning does. The rust layer formed in Qingdao possesses a higher ability to block the permeation of chloride ions than that formed in Wanning does.

Key words: low-alloy steel; weathering steel; atmospheric corrosion; marine environment; subtropical environment

[*This study was financially supported by the National Key Basic Research and Development Program of China (No.2004CB619102) and New Century Excellent Talents in China.*]

1. Introduction

It is well established that hot weather, high humidity, and pollution will accelerate the atmospheric corrosion of carbon steel and low-alloy steel. Hou and Liang [1-2] analyzed the atmospheric corrosion of 17 steels at seven different sites in China for 16 years. Finally, they found that hot weather and high humidity could result in more serious damage on these steels than sulfur dioxide and chloride ions. However, only the weight loss data were provided in their articles, without containing any information about the corrosion products and corrosion mechanism. Oh *et al.* [3] investigated the atmospheric corrosion of different steels in marine, rural, and industrial environments by Mössbauer and Raman spectroscopies and X-ray diffraction (XRD) and concluded that the carbon steel exposed at the marine site corrodes at high rate, which mainly resulted from the magnetic maghemite and large particles of goethite formed on it. In contrast, fine goethite formed on weathering steels reduced the corrosion rate in the marine, rural, and industrial sites. Ishikawa *et al.* [4] researched the rusts formed on weathering steels exposed in different environments (including coastal, industrial, urban, and mountainous environment) by gas adsorption. They concluded that the particle size and pore size in rust layers increased with the increase in environmental NaCl content. Marco *et al.* [5] studied the corrosion products formed on carbon steel after being exposed in the Antarctic (polar climate) and Easter Island (subtropic climate) using Mössbauer spectroscopy, XRD, and X-ray photoelectron spectroscopy (XPS), and found that the major constituents of the rust formed in the Antarctic environment were goethite and lepidocrocite, whereas lepidocrocite and ferrihydrite were the major constituents of the rust in the Easter Island. Weathering steel has also been investigated by the simulative corrosion test. Wang *et al.* [6] studied the atmospheric corrosion resistance of 08CuPVRE and 08CuP weathering steels. Zhang *et al.* [7-8] considered that rare earth (RE) can increase the resistance to atmospheric

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corrosion for low-alloy weathering steels but have no influence on carbon steel. Piao *et al.* [9] concluded that the combination of dry-wet circle test and electrochemical impedance spectroscopy (EIS) test would be effective to evaluate the weathering steel's corrosion-resistant performance rapidly and reasonably.

In the present study, an attempt is made to compare the effects of industrial pollution (such as sulfur dioxide) and weather factors (temperature and humidity) on the marine atmospheric corrosion of a newly developed low-alloy weathering steel. Qingdao and Wanning were chosen as two experimental sites. Qingdao is one typical temperate marine environment with industrial pollution, whereas Wanning is one typical subtropical marine environment almost without industrial pollution. The emphasis is focused on the structures and properties of corrosion products formed respectively at the two sites.

2. Experimental procedures

2.1. Material and exposure test

The newly developed low-alloy weathering steel was melt in a 25-kg vacuum induction furnace. The plate of 6 mm in thickness was obtained by means of controlling rolling followed by accelerated cooling. The chemical composition of the steel is listed in Table 1. The optical metallograph of the steel is given in Fig. 1. It shows that the matrix microstructure is refining granular bainite and quasi-polygonal ferrite, the yield strength and tensile strength of the steel are 780 and 890 MPa, respectively. The samples with a size of 100 mm×50 mm×5 mm were exposed in Qingdao and Wanning. The test panels were exposed at an angle of 45° to the ground and facing south. The major meteorological data of the atmosphere are given in Table 2, and the corrosive factors of the atmosphere are given in Table 3.

Table 1. Chemical composition of the steel wt%

C	Si	Mn	S	Cu	Cr	Ni	Nb	Mo	B	Al	P
0.028	0.38	1.5	0.007	0.79	0.58	0.59	0.19	0.3	0.0017	0.061	0.086

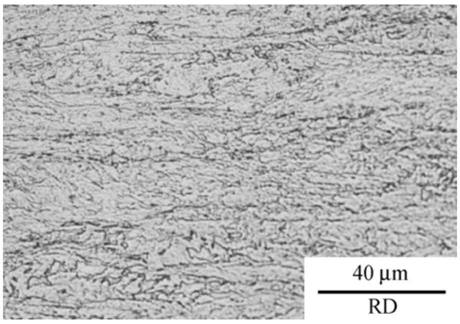

Fig. 1. Optical metallograph of the newly developed low-alloy weathering steel (RD represents the rolling direction).

All procedures were in accordance with ISO-DIS 8565 [10].

2.2. Analysis of the rust layer

Quantitative analysis of the rust phase composition was carried out by using an internal standard method of XRD and a Cu target was used. The scanning speed was 2.0°/min, the 2θ angle was in a range from 10° to 50°. ZnO was used as the internal standard matter. The crystalline phases of the rust were confirmed to be Goethite (α-FeOOH), akaganeite (β-FeOOH), lepidocrocite (γ-FeOOH), and magnetite (Fe_3O_4). The diffraction intensities of (011) reflection of α-FeOOH, (110) reflection of β-FeOOH, (020) reflection of γ-FeOOH, and (220) reflection of Fe_3O_4 were measured and referred to (100) reflection of ZnO powder. The ZnO were mixed with the same ratio of 30% to the corrosion products.

The adsorption curves of N_2 on the rusts were volumetrically measured at the boiling point of liquid N_2 to study the pore structures of the rust layer.

Table 2. Meteorological data of the atmosphere at Qingdao and Wanning

Site	Average temperature /°C	Average humidity / %	Precipitation / ($mm \cdot a^{-1}$)	Distance to sea / m
Qingdao	12.5	71	643	5
Wanning	24.6	86	1563	350

Table 3. Corrosive factors of the atmosphere at Qingdao and Wanning

site	Cl^- deposition / ($mg \cdot dm^{-2} \cdot d^{-1}$)	SO_2 deposition / ($mg \cdot dm^{-2} \cdot d^{-1}$)	Rain pH
Qingdao	0.250	0.704	6.1
Wanning	0.387	0.060	5.0

Polarization curves and EIS measurements were carried out in a 0.5wt% NaCl solution. All potentials were measured by using a saturated calomel electrode (SCE) as reference and by using platinum as assistant. Polarization curve measurements were taken at a sweep rate of 10 mV/min. EIS measurements were carried out at a frequency range from 100 kHz to 10 mHz and an applied voltage of 10 mV.

3. Results

3.1. Weight loss

Fig. 2 shows the thickness loss of the tested steels after being exposed in Qingdao and Wanning for one year. The thickness loss of the steel in Wanning is twice more than that in Qingdao. The thickness loss was calculated by the following formula:

$$d=W/(\rho A) \qquad (1)$$

where d is the thickness loss, W the weight reduction, ρ the density of the steel (7.8 g/cm^3), and A the surface area of the specimen.

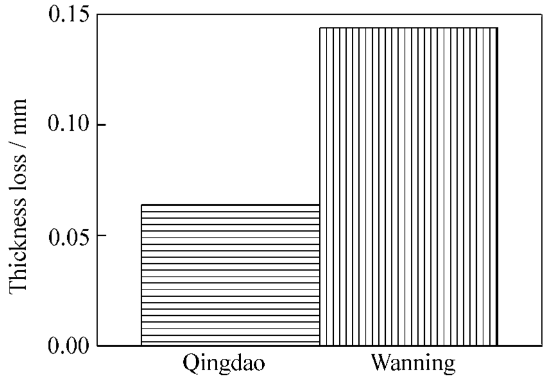

Fig. 2. Thickness loss of the tested weathering steels after being exposed in Qingdao and Wanning for one year.

3.2. Constituent compounds of the rust

From Fig. 3, the rust layer are composed of α-FeOOH, β-FeOOH, γ-FeOOH, Fe_3O_4, and X-ray amorphous compounds, which are mainly microcrystalline oxides or hydroxides and can not be identified by XRD. α-FeOOH [11] and X-ray amorphous compounds [12-13] are nonactive in the corrosion process. Both γ-FeOOH [11, 14] and β-FeOOH [15] can act as accelerating agents and promote the electrochemical corrosion process. β-FeOOH works as a reservoir of chloride and the rust layer becomes porous [16], and then chloride ions can move through the rust layer and arrive at metal surfaces easily [17]. However, fine microcrystalline oxides or hydroxides may fill in pores formed in the rust layer. Thus, the rust layer with a higher content of X-ray amorphous compounds will be more compact. The contents of β-FeOOH, γ-FeOOH, and Fe_3O_4 in Wanning are more than those in Qingdao, but the contents of α-FeOOH and X-ray amorphous compounds in Wanning are less than those in Qingdao because the atmosphere containing sulfur dioxide promotes the phase transformation rate of γ-FeOOH into X-ray amorphous compounds [18] and α-FeOOH [19].

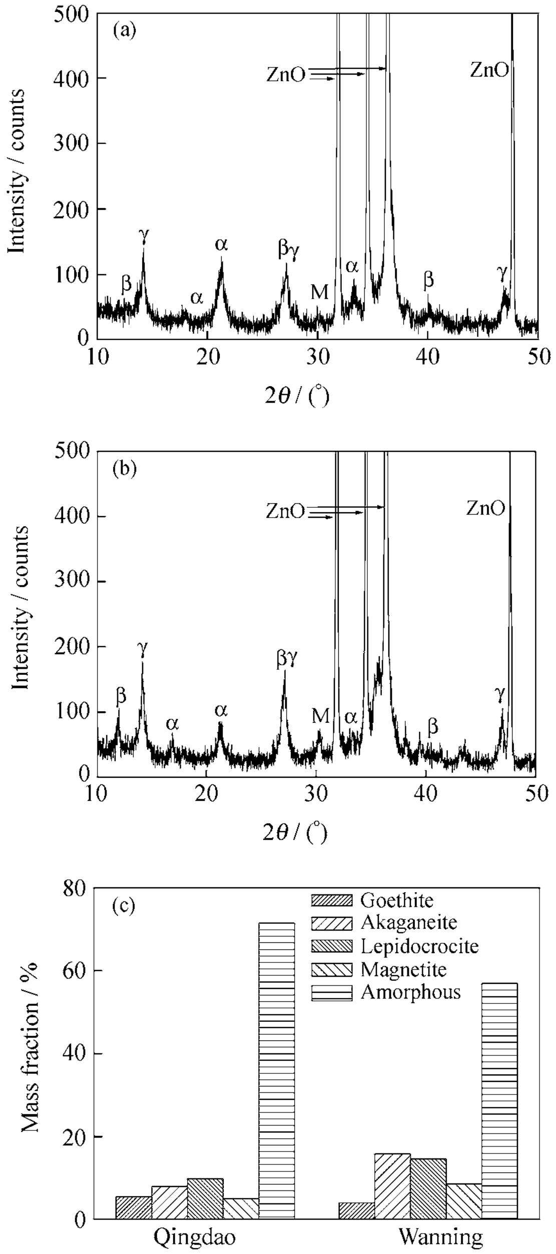

Fig. 3. XRD results of the rust phase composition of the steels after being exposed in Qingdao (a) and Wanning (b) for one year and the mass fraction of different rust phases (c). α—Goethite; β—Akaganeite; γ—Lepidocrocite; M—Magnetite; Amorphous—X-ray amorphous compounds.

3.3. Morphology of the rust layer and distribution of alloying elements

The surface micrographs of the rust layer formed on the steels after being exposed in Qingdao and Wanning for one year are shown in Fig. 4. The rust layer formed in Qingdao is granular and compact, whereas that formed in Wanning is lamellar and loose. The size of the former unitized granule is about 25 μm, whereas the size of the latter unitized block is about 50 μm. In term of the present observations, the rust layer formed in Qingdao is composed of smaller particles and is more compact than that formed in Wanning.

Fig. 5 is the cross-section micrographs and the EDS result of the rust layer formed on the steels after being exposed in Qingdao and Wanning for one year. It is found that the Cr content in the rust layer near the steel matrix is higher than that far from the steel matrix in Qingdao, but this case is not obvious in Wanning. Also, the Cu content in the rust layer near the steel matrix is higher than that far from the steel matrix, whereas this case is more obvious in Qingdao than in Wanning.

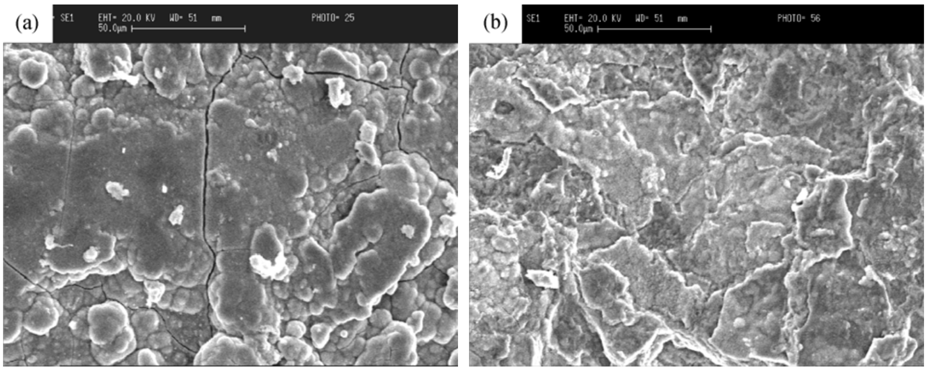

Fig. 4. Surface micrographs of the rust layer formed on the steels after being exposed in Qingdao (a) and Wanning (b) for one year by SEM.

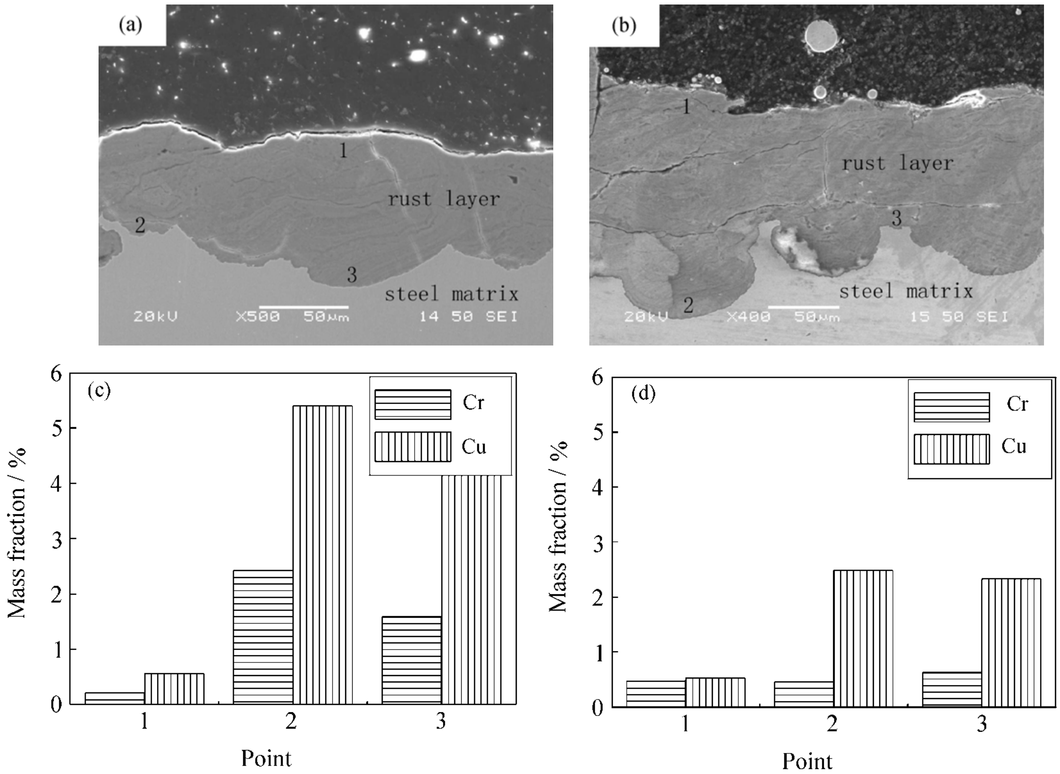

Fig. 5. Cross-section micrographs of the rust layer formed on the steels after being exposed in Qingdao (a) and Wanning (b) for one year by SEM, and distributions of Cr and Cu at points 1, 2, and 3 in the cross section of the rust layer formed on the steels after exposing in Qingdao (c) and Wanning (d) for one year by EDS.

3.4. Pore structure of the rust layer

Fig. 6 depicts the adsorption curves of N_2 on the rust formed on the steels after being exposed in Qingdao and Wanning for one year. The adsorbed amount of N_2 on the rust formed in Qingdao is more than that in Wanning. All the N_2 isotherms belong to the type 2 of the Brunauer-Deming-Deming-Teller classification, and they rise steeply at a low relative pressure (p/p^0), indicating the existence of micropores in the rusts. The rust with a larger adsorption amount consists of smaller particles and pores [4]. Thus, the rust formed in Qingdao consists of smaller particles and pores than that formed in Wanning.

An agglomerate of smaller particles exhibits a higher specific surface area [4]. The specific surface area of N_2, designated as SA(n), was evaluated from the adsorption isotherms of N_2 by the Brunauer-Emmett-Teller (BET) method using a cross-sectional area of N_2 molecules (0.162 nm^2). The SA(n) values of the rust formed in Qingdao and Wanning are 97.8040 and 75.3436 m^2/g, respectively. The average pore widths by the BET method of the rust formed in Qingdao and Wanning are 39.9857 and 43.8256 nm, respectively.

These three results indicate that the rust layer formed in Qingdao is an agglomerate of smaller particles and has smaller pores than that formed in Wanning, so the former is more compact than the latter.

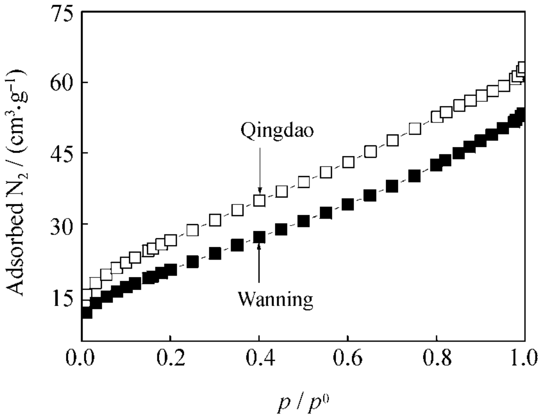

Fig. 6. Adsorption curves of N_2 on the rusts formed on the steels after being exposed in Qingdao and Wanning for one year.

3.5. Polarization behavior of the steel with a rust layer

Fig. 7 shows the polarization curves of the steels with a rust layer after being exposed in Qingdao and Wanning for one year. The free corrosion potential of the sample exposed in Qingdao is higher than that in Wanning, whereas the anodic and cathodic currents of the sample in Qingdao are less than those in Wanning. This fact indicates that the rust layer formed in Qingdao suppresses the anodic and cathodic reaction more remarkably than that formed in Wanning.

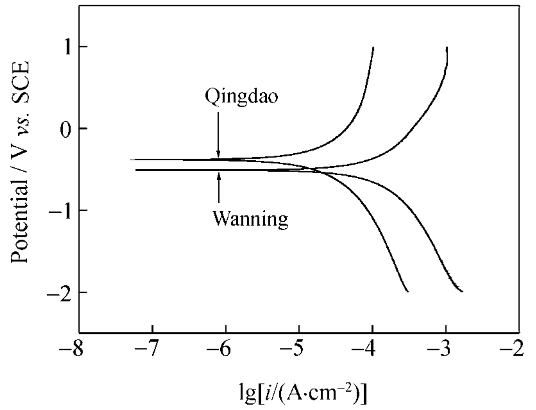

Fig. 7. Polarization curves of the steel with a rust layer in a 0.5wt% NaCl solution (the steel had been exposed in Qingdao and Wanning for one year).

3.6. EIS of the steels with a rust layer

Fig. 8 shows the Nyquist diagrams of the steels with a rust layer after being exposed in Qiangdao and Wanning for one year. The equivalent electrical circuit (as shown in Fig. 9) is proposed to simulate the electrochemical process of the steel. Here, Wang *et al.* [20] and Zhang *et al.* [21] used W (Warburg impedance) at low frequencies in the equivalent electrical circuit, and W was a straight line with an angle of 45° to the ReZ axis, while Fig. 8 shows that the diffusion tail at low frequencies is about 25° to the ReZ axis. So the diffusion impedance Z_D, proposed by Bousselmi *et al.* [22-23] and Santana Rodriguez *et al.* [24], is more properly. Z_D was defined in Ref. [22].

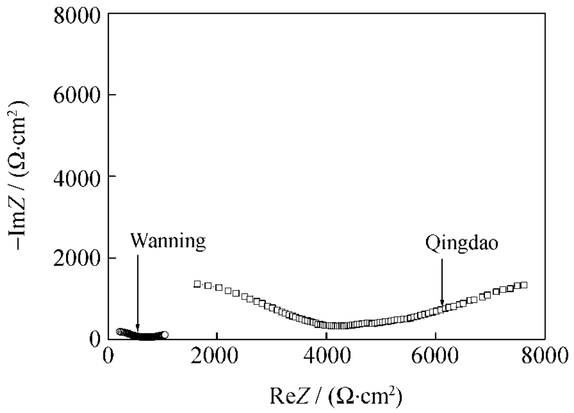

Fig. 8. Nyquist diagrams of the steel with a rust layer in a 0.5wt% NaCl solution (the steel had been exposed in Qingdao and Wanning for one year).

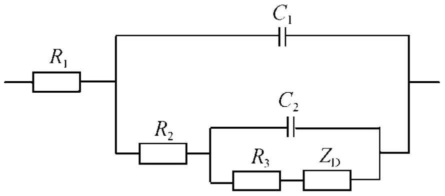

Fig. 9. Equivalent electrical circuit for a steel/rust layer/NaCl solution interphase: R_1—resistance of the electrode solution; R_2—resistance of the rust layer; C_1 and C_2—capacitances of the rust layer and the double layers, respectively; R_3—charge transfer resistance; Z_D—impedance associated with diffusion.

As the electric resistance of the rust compounds (oxide or hydroxide) is generally very high, R_2 (the resistance of the rust layer) represents the barrier against the migration of ions in association with the corrosion reaction and it is the key parameter for estimating the protective properties of the rust layer.

The rust layer resistances of the samples in Qingdao and Wanning, which are deduced from this proposed equivalent electrical circuit, are 2513 Ω·cm^2 and 333.5 Ω·cm^2, respectively. This fact indicates that the former has a higher ability to block the permeation of chloride ions than the latter.

4. Discussion

The steel corroded more seriously in Wanning than in Qingdao, the thickness loss of the steel in Wanning is twice more than that in Qingdao. Temperature, humidity, and precipitation in Wanning are higher than those in Qingdao, whereas the industrial pollution in Wanning is lower than in Qingdao. These facts indicate that the combination of hot weather, high humidity, and high precipitation along with chloride ions in subtropical marine environment produces more intensive corrosion than the combination of sulfur dioxide pollution along with chloride ions in temperate marine environment does.

The rust layer formed on the steel greatly affects the corrosion behavior because of various molecules and ions needed in corrosion such as O_2, H_2O, and chloride ions must move through it in the corrosion process.

The primary difference of the rust layers is that the content of X-ray amorphous compounds of the rust formed in Qingdao is more than that formed in Wanning. The X-ray amorphous compounds are mainly some fine particles including Fe_3O_4, γ-Fe_2O_3, or α-FeOOH, which are nonactive in the corrosion process [12-13]. At the same time, the X-ray amorphous compounds can make the rust layer compact. Through the scanning electron micrographs of the rust layers, the rust layer formed in Qingdao is composed of smaller particles and is more compact than that formed in Wanning. Both the adsorption amount of N_2 and the SA(n) of the rust formed in Qingdao are higher than those formed in Wanning, whereas the average pore size of the rust formed in Qingdao is smaller than that formed in Wanning. These facts indicate that the rust layer formed in Qingdao is an agglomerate of smaller particles and contains smaller pores than that formed in Wanning so that it is more compact than that formed in Wanning. Thus, the rust layer formed in Qingdao has a higher ability to block the permeation of chloride ions than that formed in Wanning, which can also be deduced from EIS.

The average size of rust particles increases with the number of dissolution-crystallization processes since the particles that were only partially dissolved during wetting can grow further during drying by nucleating around the particles, one wet-dry cycle after another wet-dry cycle [5]. The combination of hot weather, high humidity, and high precipitation in Wanning can increase the number of wet-dry cycles, which can promote the size growth of rust particles and make the rust layer porous.

In marine atmosphere, NaCl promotes rust particles to grow, resulting in the formation of voids among larger particles in the rust layer and facilitating further corrosion [4]. It is generally believed that the atmosphere corrosion of steels is more serious in industrial environment than in rural environment due to contamination such as sulfur dioxide and nitrogen dioxide. However, in coastal zones, it has been pointed out that sulfur dioxide interferes with the particle growth and is possibly beneficial to the corrosion resistance of steels [4, 24]. By the present investigation, it is suggested that one competitive adsorption process occurs between chloride ions and sulfur compounds, and then the effect of chloride ions is weakened. Thus, it is possible that sulfur dioxide promotes the rust layer to be more compact in marine atmosphere.

Both the Cr content and the Cu content are higher in the rust layer near the steel matrix than those far from the steel matrix. The phenomena are more obvious in Qingdao than in Wanning. Cr [13, 21] and Cu [13, 25] can enhance the corrosion resistance of weathering steel. It is reasonable to presume that the enrichment of Cr and Cu in rust layers involves a diffusion process. Because a slower corrosion occurs in Qingdao, Cr and Cu get more time to diffuse into the rust layer near the steel matrix. On the other hand, the enrichment of Cr and Cu near the steel matrix slows down corrosion further. This is the possible reason that makes different enrichment degrees of Cr and Cu between Qingdao and Wanning. It is an additional reason that the rust formed in Qingdao suppressed corrosion more remarkably than the rust formed in Wanning.

5. Conclusions

(1) The steel corroded more seriously in Wanning than in Qingdao. The combination of hot weather, high humidity, and high precipitation along with chloride ions in subtropical marine environment brings about more serious corrosion than the combination of sulfur dioxide pollution along with chloride ions in temperate marine environment does.

(2) Compared with the rust layer formed in Wanning, the rust layer formed in Qingdao is composed of smaller particles and smaller pores. Its ability to block the permeation of chloride ions is higher than that of the rust layer formed in Wanning.

(3) Cr and Cu are enriched in the rust layer near the steel matrix, which is more obvious for the samples tested in Qingdao than those tested in Wanning. The enrichment can reduce the corrosion rate. This is an-

other reason for the slower corrosion of the steel in Qingdao than in Wanning.

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