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Initial atmospheric corrosion of Zinc sprayed with NaCl①

QU Qing(屈 庆)[1,2], YAN Chuan-wei(严川伟)[2], ZHANG Lei(张 蕾)[2],
LIU Guang-heng(刘光恒)[1], CAO Chu-nan(曹楚南)[2]
(1. Department of Chemistry, Yunnan University, Kunming 650091, China;
2. State Key Laboratory for Corrosion and Protection, Institute of Metal Research,
The Chinese Academy of Sciences, Shenyang 110016, China)

Abstract: Regularities of the initial atmospheric corrosion of zinc sprayed with different amount of NaCl exposed to air at 80% relative humidity and 25 ℃ were investigated via quartz crystal microbalance in laboratory. The results show that NaCl can accelerate the corrosion of zinc. Mass gain of zinc increases with the exposure time increasing, which can be correlated by using exponential decay function. The relationship between mass gain and amount of NaCl sprayed at a certain exposure time follows a quadratic function. Meanwhile, Fourier transform infrared spectroscopy, X-ray diffraction, scanning electron microscopy and electron dispersion X-ray analysis were used to characterize the corrosion surface and products. $Zn_5(OH)_8Cl_2 \cdot H_2O$ and ZnO are the dominant corrosion products, which unevenly distribute on the surface of zinc in the presence of NaCl. A probable mechanism is simply presented to explain the experimental results.

Key words: initial atmospheric corrosion; corrosion regularity; quartz crystal microbalance
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1 INTRODUCTION

As a main accelerator of atmospheric corrosion of metals in marine environments, sodium chloride, NaCl, can absorb water vapor from humid air to form thin water film on the metal surface. The role of this water layer is to provide a medium for mobilization of ions. NaCl dissolved in the layer also considerably raises the conductivity of the electrolyte. This will greatly increase the electrochemical corrosion and affect the composition of the corrosion products. It is therefore of great interest to study the effect of NaCl on the atmospheric corrosion of metals. In recent years, the atmospheric corrosion of metals in the presence of NaCl has been addressed in field as well as in laboratory in controlled environments[1－9]. All of researchers demonstrate that NaCl can enhance the corrosion rate of metals. Nevertheless, few of them have investigated the regularities of the initial atmospheric corrosion of zinc in the presence of NaCl due to measurement difficulties. But the information of the initial atmospheric corrosion is very important and helpful to understand the corrosion mechanism. With the development of highly sensitive instrument quartz crystal microbalance (QCM) in recent years, corrosion effects can be observed after several hours' exposure. And it is possible to study the initial atmospheric corrosion in the presence of NaCl. In the present work, the regularities of the initial atmospheric corrosion of zinc sprayed with different amount NaCl exposed to air at 80% RH(relative humidity) and 25 ℃ based on the experimental data which are investigated by means of QCM. The corrosion surfaces of zinc were characterized by X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, scanning electron microscopy (SEM) and electron dispersion X-ray analysis.

2 EXPERIMENTAL

The equipment used in the experiments was described in detail elsewhere[10]. It was made entirely of glass and Teflon. The RH was kept at (80±2)% which was regulated by mixing flows of dry air and the air saturated with water vapor at 60 ℃. And the experimental temperature was kept at 25 ℃ in the whole test process by means of a thermostatically controlled water tank. The environmental temperature was kept at 25±1 ℃ to avoid condensation in the parts of the system outside the water tank.

To study the initial atmospheric corrosion of zinc, The QCM (EG&G) with a sensitivity better than 10^{-8} g/cm^2 was applied to measure in situ the small mass changes of zinc. The QCM method for mass change monitoring is based on the inverse piezoelectric effect, discovered in 1880 by Pierre and Jacques Curie, in which a voltage is applied to an

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Correspondence: QU Qing, Lecturer, PhD; Tel: +86-871-5032306; E-mail: quqing@ynu.edu.cn

ionic crystalline solid, such as quartz, to produce physical distortions for the crystal. Piezoelectric materials have been used as stable oscillator, and it was soon recognized that the addition of mass to an oscillator would change its frequency. For rigid deposits, the change in resonant frequency of the oscillating crystal(Δf) is proportional to the change in mass per unit area($\Delta m/A$) of the working electrode. As long as Δf is less than a few percent of the resonant frequency of crystal, the linear relation between Δf and $\Delta m/A$ is constant. The equation is expressed as[11, 12].

$$\Delta f = -2\Delta m(f_0)^2/(nA\sqrt{G\rho}) \qquad (1)$$

Where f_0 is the fundamental frequency of the crystal, n is order of the harmonic (for rigid deposits, $n = 1$), G is the shear modulus of quartz (2.94×10^{11} Pa), and ρ is the density of quartz, 2.648 g/cm^3. Thus, for a 9MHz crystal operating in the fundamental mode, Eqn. (1) can be rewritten as

$$\Delta m/A = -5.45\Delta f \qquad (2)$$

Platinum was sprayed on each side of the AT-cut quartz crystal disk to form circular electrodes with an area of 0.2 cm^2 and a thickness of around 300 μm. Before plating zinc, the electrodes were rinsed in ethanol and dried with warm air. Then zinc was plated in an acid bath to one side of the platinum disk of the AT-cut quartz crystal with a thickness of 1.3 μm. The purity of platinum and zinc used for the QCM electrodes is 99.99%. After washed with ethanol and dried with a hair drier, they were stored in a desiccator. The surface of the electrode is uniform. Salt was deposited on the sample surface by spraying NaCl solution with different percent of ethanol saturated. The distribution of salt on the surface after spraying was quite even, which can be proved by using SEM. The sprayed amount of NaCl was determined directly by means of QCM. 5.0, 15.0, 30.0, 45.0 μg/cm^2 NaCl were used at 80% RH in the experiments. The samples had been stored drily for about 12 h before the start of exposure experiment. All the mass gain of zinc had subtracted the amount of NaCl deposition. Corrosion products were analyzed by SEM/EDAX (XL-30PHILIPS), XRD (PW1700) and FTIR (Magna-IR 560).

3 RESULTS AND DISCUSSION

As NaCl can easily absorb water vapor from humid air, part of the initial mass gain of zinc may be caused by the absorbed water. In order to find out the effect of absorbed water on the initial mass gain of zinc, zinc covered and uncovered quartz crystals were respectively studied, which were deposited with 25.8 μg/cm^2 NaCl and exposed to air at 80% RH and 25 ℃. The results are shown in Fig. 1. As can be seen from this figure, the amount of water absorbed by 25.8 μg/cm^2 NaCl on zinc uncovered quartz crystal really leads to the mass change, but it can be almost ignored comparing to that of zinc covered quartz crystal. That is, the water absorbing by NaCl depositing on zinc surface is not the main part of the mass gain.

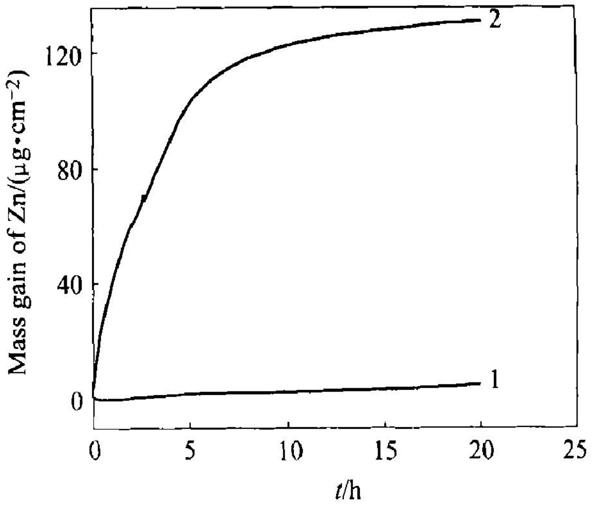

Fig. 1 Mass changes of Zn uncovered quartz and Zn covered quartz vs exposure time at 80% RH and 25 ℃

1 —Zn uncovered quartz sprayed 25.8 μg/cm^2 NaCl;
2 —Zn covered quartz sprayed 25.8 μg/cm^2 NaCl

Fig. 2 shows the relation between the mass gain of zinc and the exposure time at 80% RH and 25 ℃. The mass gain of zinc is seen to increase with the exposure time increasing, but it doesn't change obviously after some time's exposure in the presence of moderate to high amount NaCl spraying. The relationship between mass gain of zinc and exposure time can be correlated by means of exponential decay function

$$\Delta m/A = B + D \cdot \exp[(t_0 - t)/k] \qquad (3)$$

where B, D, k are constants which can describe the corrosion tendency; D and k are determined by

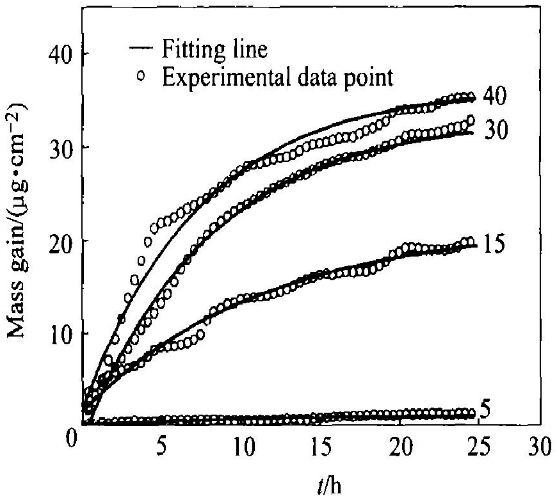

Fig. 2 Mass gain vs exposure time of zinc sprayed with NaCl in pure air at 80% RH and 25 ℃

the chemical characteristic of the metal surface; The smaller the values of D and k, the more obviously the corrosion rate abates in the later. B is connected to the amount of NaCl deposition. The mass gain accelerates with the B value, and Table 1 shows that B is related to the square of the amount of NaCl sprayed. $\Delta m/A$ is the mass gain per unit area of zinc ($\mu g/cm^2$), t is the measure time, and t_0 is the beginning time of measurement. In this paper, t_0 is 0. All the experimental data at different amount of NaCl was correlated on the basis of Eqn. (3). The regression value of B, D, k and the sum of the squares of the deviation of the theoretical curve from the experimental points (ΣSD) obtained by means of in Eqn. (3) were listed in Table 1. As can be seen from Fig. 2 and the ΣSD in Table 1, Eqn. (3) can be applied to correlate the experimental data.

Table 1 Regression value of B, D, k and ΣSD

NaCl content/ ($\mu g \cdot cm^{-2}$)	B	D	k	ΣSD
5.0	1.316	−1.262	44886.38	0.015
15.0	21.659	−20.245	40752.45	0.583
30.0	33.089	−34.736	28592.07	0.463
45.0	36.441	−34.825	26792.63	1.810

Fig. 2 indicates that the mass gain of zinc also increases with the amount of NaCl increasing, but corrosion rate in the later will abate in the presence of higher amount of NaCl spraying. This can be explained by using the electrochemical process that takes place on the surface of zinc. This mechanism can be summarized as follows: In the early stages of the corrosion process, when the surface of zinc is wet, the anodic dissolution of zinc is balanced by oxygen reduction in the catholic areas.

$$Zn \longrightarrow Zn^{2+} + 2e \tag{4}$$

$$1/2O_2 + H_2O + 2e \longrightarrow 2OH^- \tag{5}$$

Therefore, countless electrochemical cells begin to form on the surface of zinc, the water film on zinc will present weak basicity while OH^- forms. The addition of NaCl may lead to the formation of an electrolyte film rather quickly, and the conductivity of the electrolyte film increases with the amount of NaCl deposition increasing. With the reaction going on, cations, e.g. Na^+ (aq), will migrate towards the catholic areas while anions, e.g. Cl^- will move towards the zinc dissolution sites, where the insoluble $Zn_5(OH)_8Cl_2 \cdot H_2O$ forms gradually as

$$4ZnO(s) + Zn^{2+}(aq) + 5H_2O + 2Cl^-(aq) \longrightarrow Zn_5(OH)_8Cl_2 \cdot H_2O(s) \tag{6}$$

This is in agreement with the stability diagram of $Zn_5(OH)_8Cl_2 \cdot H_2O$[13], which indicates that $Zn_5(OH)_8Cl_2 \cdot H_2O$ is stable at intermediate pH and relatively high chloride activities. In the cathodic areas where chloride activities are low and pH value is high, ZnO tends to form. Therefore, $Zn_5(OH)_8Cl_2 \cdot H_2O$ is expected to precipitate close to the anodic sites. The higher the chloride activities, the more easily $Zn_5(OH)_8Cl_2 \cdot H_2O$ forms. Formation of the insoluble products is unfavorable to oxygen diffusion, so the subsequent corrosion of zinc becomes more difficult, and the corrosion of zinc in the later will decrease.

The electrochemical nature of the atmospheric corrosion of zinc in the presence of NaCl is apparent from the localized nature of the corrosion attack, which can be confirmed by Fig. 3. Fig. 3 gives the SEM morphology of the 21.43 $\mu g/cm^2$ NaCl-treated sample after exposure to air at 80% RH and 25 ℃. The corrosion products on the surface of the NaCl-treated zinc are obviously uneven. The respective EDAX of NaCl-treated samples after exposure indicates that the elements Zn, O and Cl, etc were present in the club-shaped products area while no Cl element was found in the poor-crystalloid products area. The uneven distribution of chloride is due to the migration of aqueous ions in the electrical field established between anodic and cathodic areas on zinc surface.

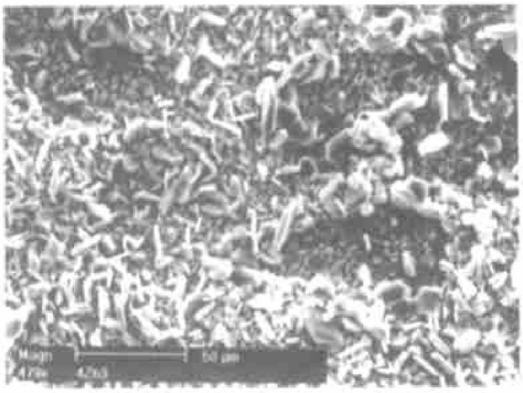

Fig. 3 SEM morphologies of the NaCl-treated sample

As can be seen from Fig. 4, analysis of the samples by XRD under the experimental condition revealed that $Zn_5Cl_2(OH)_8 \cdot H_2O$ and ZnO, ZnO were the main corrosion products. And it was also confirmed by FTIR spectroscopy that $Zn_5(OH)_8Cl_2 \cdot H_2O$ existed in the products. ZnO, $Zn_5(CO_3)_2(OH)_6$ and $Zn_5(OH)_8Cl_2 \cdot H_2O$ are used as the relevant reference compounds. The different reference compounds have characteristic absorption bands at different positions[14]. ZnO only has the bands in the 350 cm^{-1} to 600 cm^{-1} region corresponds to the zinc-oxygen bond. $Zn_5(OH)_8Cl_2 \cdot H_2O$ has strong bands at 3 450 cm^{-1} and weak bands at 1 620 cm^{-1}, 900 cm^{-1} and 730 cm^{-1}. $Zn_5(CO_3)_2(OH)_6$ has the strong bands at 1 380 cm^{-1} and 1 510 cm^{-1}, corresponding to the asymmetric stretching vibrations of carbonate ion, and

$Zn_5(CO_3)_2(OH)_6$ also has weak bands at 1 040 cm^{-1}, 830 cm^{-1}, 735 cm^{-1} and 675 cm^{-1}. Corrosion products formed on confined zinc surfaces, which was sprayed with 45 $\mu g/cm^2$ NaCl and exposed to air for 25 h, are presented in Fig. 5. Fig. 5 shows that the corrosion products have the bands at 3 450 cm^{-1}, 1 625 cm^{-1}, 1 380 cm^{-1}, 1 510 cm^{-1}, 900 cm^{-1}, 1 040 cm^{-1}, 830 cm^{-1}, 730 cm^{-1} etc. Therefore $Zn_5Cl_2(OH)_8\cdot H_2O$ and $Zn_5(CO_3)_2(OH)_6$ may exist in the corrosion products. Due to the spectra in the experiment were obtained in the region from 650 cm^{-1} to 4000 cm^{-1}, nature bands of ZnO cannot be detected by using FTIR in this paper. Furthermore, due to the air used in the experimental has been cleaned, only little amount of CO_2 presents in the air, $Zn_5(CO_3)_2(OH)_6$ formed on the corrosion products is so little that it cannot be detected by XRD.

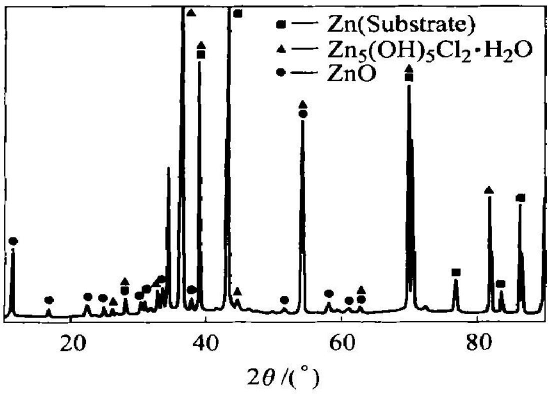

Fig. 4 XRD patterns of the corrosion products on the NaCl treated zinc exposed to air

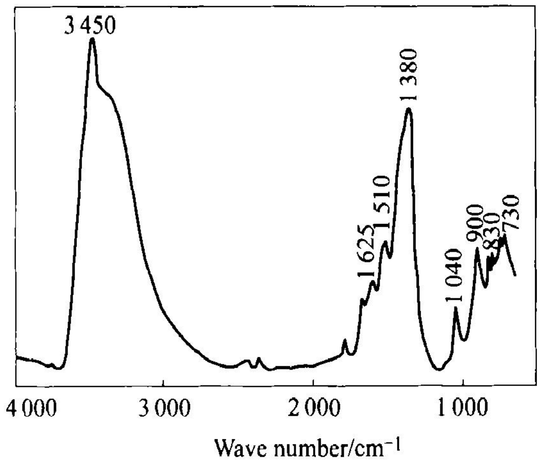

Fig. 5 FTIR spectra of the corrosion products on confined zinc surface sprayed with 45 $\mu g/cm^2$ NaCl after 25 h exposure to air at 80% RH and 25 ℃

5 CONCLUSIONS

The effects of NaCl on the initial atmospheric corrosion of zinc can be well investigated by QCM in laboratory. NaCl dissolved in the absorbed water of the zinc surface gives rise to electrochemical corrosion. The corrosion products unevenly distribute on the surface of zinc in the presence of NaCl. $Zn_5(OH)_8Cl_2\cdot H_2O$ and ZnO are the dominant corrosion products. Mass gain of zinc increases with the amount of NaCl increasing, which follows a quadratic function. Mass gain of zinc also increases with the exposure time increasing, which can be correlated by an exponential decay function.

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