



Initial corrosion behavior of pure zinc in simulated tropical marine atmosphere

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Received 2 November 2017; accepted 3 June 2018

Abstract: The initial corrosion behavior of pure zinc in a simulated tropical marine atmosphere was investigated using gravimetric method, scanning electron microscope combined with energy dispersive spectroscopy (SEM-EDS), X-ray diffractometry (XRD), Fourier transform infrared spectrometry (FTIR) and electrochemical impedance spectroscopy (EIS). The kinetics of corrosion process is a decelerating process following the empirical equation $D=At^n$ ($n<1$). The protectiveness of the corrosion product layer could be attributed to the formation of simonkolleite, $Zn_5(OH)_8Cl_2 \cdot H_2O$, which could inhibit the rate determining step, namely charge transfer step, of the electrochemical corrosion process. A model of the evolution process of the product layers formed on zinc was proposed. In addition, the regularity of the corrosion rate of zinc as a function of the NaCl deposition rate can be described by a power function.

Key words: zinc; corrosion kinetics; corrosion product; electrochemical impedance spectroscopy (EIS); simonkolleite

1 Introduction

Zinc is an important structural metal and it has been extensively used in many fields, which follows after iron, aluminum and copper [1]. Because of its good corrosion resistance and relatively low price, approximately half of zinc is used to protect steel from corrosion. As one of the metals regularly exposed to the outdoor atmosphere, a lot of work has been performed to investigate the corrosion behaviors of zinc both in fields and controlled laboratory environments [1–24].

Atmospheric corrosion of metal is a complicated process and affected simultaneously by many environmental factors such as temperature [6,7], humidity [25–27], and contaminants [14,28]. The variation of these parameters can in turn lead to the formation of different corrosion products on metal surface. It has been shown that corrosion products play an important role in corrosion behavior of metal [29–33]. The structure and ion selective permeability of rust layer formed on steel were discussed [32,33]. The porous and

incompact structure in outer rust layer formed on weathering steel increases the corrosion rate, while the compact and low aggressive chlorine ions permeated structure in inner rust layer leads to a relatively low corrosion rate.

ODNEVALL [2] proposed a common reaction scheme for the generation of several major corrosion products of zinc formed in different environments. In marine atmosphere, hydrozincite, $Zn_5(CO_3)_2(OH)_6$, which was considered as an isolated barrier to protect zinc from corrosion, was formed instantaneously from the original zinc hydroxide layer on the zinc surface once being exposed to atmosphere. Thereafter, $Zn_5(CO_3)_2(OH)_6$ would be transformed into $Zn_5(OH)_8Cl_2 \cdot H_2O$ quickly with the sea salt deposits. If the amount of SO_4^{2-} in the ambient atmosphere cannot be neglected, gordaite, $NaZn_4Cl(OH)_6SO_4 \cdot 6H_2O$, would be formed from $Zn_5(OH)_8Cl_2 \cdot H_2O$ at last.

Other researchers reported that simonkolleite $Zn_5(OH)_8Cl_2 \cdot H_2O$, which is common corrosion product formed on zinc in Cl^- -rich environments, is more protective than other forms of zinc corrosion

products [3,30]. HOSKING et al [30] attributed the higher corrosion resistance of the Zn–Mg coatings to the ability of magnesium ions to neutralize hydroxides and then to facilitate the formation of a protective simonkolleite layer. More recently, CUI et al [3] found the corrosion products formed on zinc after two years exposure in Xisha islands with a three-layer laminated structure, in which simonkolleite was concentrated close to the bottom and contributed to the great protectiveness of the corrosion product layer. Despite the works discussed above, the roles of different corrosion products formed on zinc still need to be clarified.

The tropical marine atmosphere is recognized as an aggressive environment for metals because of the high temperature, high relative humidity (RH) and high chloride deposition rate, which provides conditions for higher corrosion rates and distinct corrosion behaviors [3,13]. It is reported that corrosion products formed during the initial corrosion stage is very important, which may influence the subsequent corrosion kinetics. In addition, the relation between the corrosion kinetics and the chloride salt deposition rate is vital for predicting the corrosion behavior of zinc exposed to marine atmosphere. The aim of this work is to clarify the evolution process of corrosion products of zinc in the initial corrosion stage in a simulated tropical marine environment, and to figure out the corrosion kinetics of zinc with various NaCl deposition rates.

2 Experimental

2.1 Sample preparation and exposure conditions

The zinc samples (99.9% in purity) with two sizes were used in this work. The 50 mm × 25 mm × 2 mm ones were for gravimetric measurement, and 10 mm × 10 mm × 2 mm ones were for electrochemical measurement. The samples for gravimetric measurement were ground to 400 mesh using SiC emery papers while the ones for electrochemical analysis were ground to 2000 mesh. In order to evaporate the water, these samples were rinsed with ethanol and finally dried in a desiccator for 48 h. After the treatment, the gravimetric specimens were weighed using analytic balance (with the precision of 0.1 mg).

The tropical marine atmosphere was simulated by a Weiss–Voetsch temperature and climatic test system. The samples were put horizontally in the test chamber and the exposure tests involved the following steps within a 24 h period: (1) wetting the samples in the corrosion chamber maintained at 30 °C and 90% RH for 1 h; (2) drying the samples in the chamber maintained at 30 °C and 60% RH for 2 h; (3) repeating the steps (1) and (2) 7 times. These climatic parameters are referred to a tropical marine site in China [3]. Before every exposure test, the

upward surfaces of zinc samples were added with 10 $\mu\text{L}/\text{cm}^2$ NaCl solution (water to alcohol volume ratio of 1:4) by a microliter syringe (the solutions were spread evenly on the surfaces by a nylon rope wetted with the same solution) and dried in an oven at 35 °C.

Different deposition rates of NaCl, 1170, 877.5, 585, 292.5 and 0 $\text{mg}/(\text{m}^2\cdot\text{d})$, were applied by contaminating the samples with different concentrations of NaCl solution and these samples were retrieved after 336 h exposure. The deposition rates of NaCl are based on the ISO 9223:1992, where the maximum NaCl deposition rate in outdoor environment is 1500 $\text{mg}/(\text{m}^2\cdot\text{d})$. The NaCl deposition rate of 1170 $\text{mg}/(\text{m}^2\cdot\text{d})$ was chosen to investigate the evolution of atmospheric corrosion process of zinc. The test samples were retrieved for analysis after 48, 96, 144, 240 and 336 h.

2.2 Mass loss measurement and analysis of corrosion products

Corrosion products formed on the zinc surface after laboratory exposure were removed by pickling the samples in a special solution (prepared by putting 100 g NH_4Cl in distilled water to make 1000 mL solution) at 70 °C for 5 min according to ISO 8407. After removal of corrosion products, the specimens were rinsed with distilled water by ultrasound, dried in warm air and put into the desiccator. After 48 h, they were weighed to determine their mass loss.

The phase compositions of the corrosion products were analyzed by using a Rigaku-D/Max–2500PC X-ray diffractometer complying a Cu target under 40 kV and 40 A with 2θ range of 10°–90° and a scanning rate of 2 (°)/min. Samples for FTIR measurements were analyzed using KBr pellet method. Spectra were obtained by adding 64 scans at 4 cm^{-1} resolution in the range from 400 to 4000 cm^{-1} . The background spectrum was obtained from a pure KBr pellet.

The samples for morphology analysis were cut into the size of approximately 20 mm × 20 mm and observed by a XL30–EFG scanning electron microscopy (SEM). In addition, the elemental composition was determined by energy dispersive spectroscopy (EDS).

2.3 EIS measurement

The electrochemical tests were performed with a PARSTAT2273 in a conventional glass cell, using a saturated calomel electrode (SCE) as reference and a Pt counter electrode. The measurements were carried out in 0.1 mol/L NaCl solution at (20±1) °C, which was stable enough and changed the property of original corrosion product layers to a minimum degree. To attain a stable open circuit potential, the samples were tested in the solution for 15 min. In electrochemical impedance spectroscopy (EIS) measurements, a sinusoidal AC

voltage of 10 mV was applied and the frequency range was from 100 kHz to 10 mHz.

3 Results and discussion

3.1 Corrosion kinetics

The corrosion kinetics of zinc can be determined by measuring the mass loss of zinc before and after exposure. In order to have a clear view of the corrosion damage, the mass loss of the zinc specimens was converted to the thickness loss. The thickness loss of the zinc specimens can be calculated by the following equation:

$$D = \frac{W_t \times 10^4}{\rho S} \quad (1)$$

where D is the thickness loss (μm), W_t is the mass loss (g), ρ is the density (7.14 g/cm^3) of the zinc and S is the exposed area (cm^2) of the specimen.

It is widely accepted that the corrosion kinetics of metal can be described by empirical equation [34,35]:

$$D = At^n \quad (2)$$

where t is exposure time (h); A and n are constants. The value of n is related to the effectiveness of corrosion product layer in protecting the metal: $n > 1$ indicates that the corrosion product layer is not protective and the corrosion process is an accelerating process; $n < 1$ means that the corrosion product layer is protective and the corrosion process is a decelerating process; $n = 1$ suggests that the corrosion rate is a constant.

Figure 1 shows the thickness loss of the zinc as a function of exposure time. Correlation coefficient R^2 demonstrates that the corrosion kinetics of zinc can be well fitted to the model in Eq. (2). It can be seen from Fig. 1 that the value of the n is 0.877, which indicates that the zinc corrosion is a decelerating process and the corrosion products formed on the zinc surface are protective to the substrate to a certain degree.

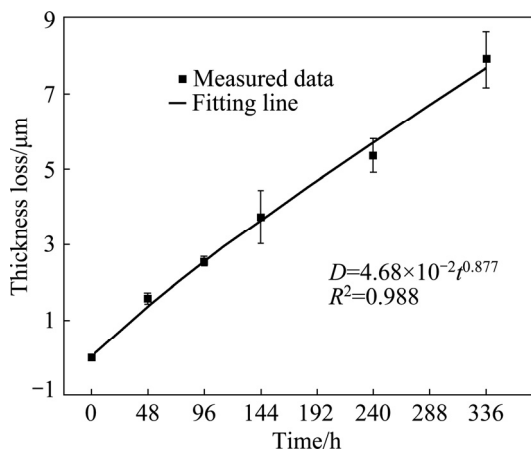


Fig. 1 Thickness loss of zinc as function of exposure time

According to Eq. (2), the instantaneous corrosion rate can be calculated using the following equation [35]:

$$R_{\text{corr}} = dD/dt = At^{n-1} \quad (3)$$

where R_{corr} is the instantaneous corrosion rate ($\mu\text{m/h}$), and A and n are obtained from the fitting results of Fig. 1. It can be seen from Fig. 2 that the corrosion rate reduces gradually with the exposure time that is consistent with the analysis of the value of n .

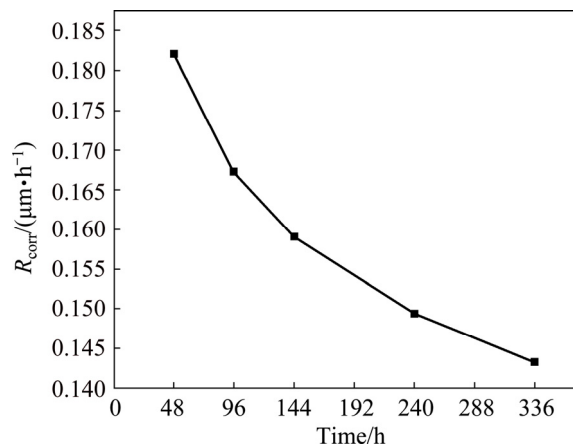


Fig. 2 Corrosion rate of zinc as function of exposure time

Figure 3 shows the thickness loss of zinc as a function of various deposition rates of NaCl. It can be seen that the corrosion rates of zinc increase dramatically with the increase of the NaCl deposition rates, and the relation between them can be described as a power function [7]:

$$D = Bx^C + D_0 \quad (4)$$

where D_0 is the thickness loss of metal without salt deposits, x is the deposition rate of salts, and B and C are constants which can describe the corrosion tendency of salinity under a certain climate condition. The correlation coefficient R^2 is very high, which indicates the goodness

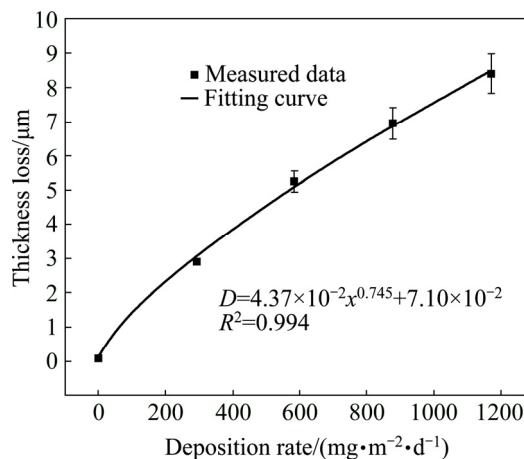


Fig. 3 Thickness loss of zinc as function of deposition rate of NaCl

of fit. Once deposition rate of the salts is confirmed, this model may be very useful in the unpolluted marine atmosphere to estimate the corrosion damage of zinc.

3.2 Composition of corrosion products

Figure 4 displays the XRD patterns for the corrosion products formed on zinc surface after various exposure time. It is revealed that the main corrosion products comprise of simonkolleite, $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ and zinc hydroxide, $\text{Zn}(\text{OH})_2$. The peaks of these compounds are sharp and intense, showing good agreement with the standard data obtained from the database. In addition, the XRD results indicate that there is also trace amount of hydrozincite, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$, on the surface. The corrosion products formed after 336 h exposure were also analyzed by the FTIR spectroscopy, as shown in Fig. 5 which confirms the existence of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ and $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ [12,28,36]. The band around 3450 cm^{-1} is due to stretching vibrations of hydroxyl groups. The peaks at 905, 710 and 466 cm^{-1} can be attributed to the vibration of $\text{Zn}-\text{O}-\text{H}$ in $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$. The peak at 1636 cm^{-1} results from the deformation vibration of crystal water. The band found at 1497 cm^{-1} with a shoulder band at 1384 cm^{-1}

and the peaks found at 1044 and 837 cm^{-1} are caused by the vibration of carbonate in $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$. In addition, the band found around 524 cm^{-1} is due to ZnO , which corresponds to the $\text{Zn}-\text{O}$ bond.

3.3 Corrosion morphology

Figure 6 shows the surface morphology of corrosion products formed on zinc for various exposure time. After 48 h of exposure, the surface is covered by the corrosion products with some network-like compounds (Figs. 6(a) and (b)). As the exposure extends, some laminar products emerge, which are distributed mainly in the protuberances (Figs. 6(c) and (d)). In the following exposure periods, thick laminar corrosion products are formed and connected with each other like ridges (Figs. 6(e)–(h)), which seems to be more compact than the network-like layer.

EDS was carried out to clarify the element compositions of the corrosion products at the marked points in Figs. 6(b), (d) and (h). The results are summarized in Table 1. It can be seen from Table 1 that the elements detected in porous net-like products are Zn, O and C, which suggests that the porous network-like products are $\text{Zn}(\text{OH})_2$ or $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$. In contrast, the relatively compact laminar products contain only Zn, O, Cl and the content of the Cl is consistent with that of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$, which indicates that the laminar products are $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$.

Observation of cross-sectional images of samples for various exposure time of zinc in different regions shows that there are two different structures of the corrosion product layers formed on the zinc surface: porous layers (PLs) and compact layers (CLs). Two typical types of the corrosion product layers of cross-sectional images of zinc samples for 48 and 336 h exposure are shown in Fig. 7. Chemical compositions of the points marked in Fig. 7 are listed in Table 2. Each of the point-marked area contains the same four elements, Zn, O, Cl and C. It can be found that the contents of Zn, O and C elements only show slight changes in the corrosion product layer throughout the whole exposure time. However, there are relatively notable differences in the content of element Cl. It is worth nothing that the element Cl is richer in the CLs (Points *b*, *d*, *e*, *f* and *g* in Fig. 7) than in the PLs (Points *a* and *c* in Fig. 7). That is to say, CLs in this test contain more $\text{Zn}-\text{O}-\text{Cl}$ phases, which is supposed to be $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$, than PLs. It is thus reasonable to preliminarily speculate that the PLs formed on zinc is due to the formation of corrosion product, $\text{Zn}(\text{OH})_2$ or $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$. PL has less protectiveness against the corrosion attack as the corrosive media can be transported to the metal surface more easily through the cracks and pores in the layer.

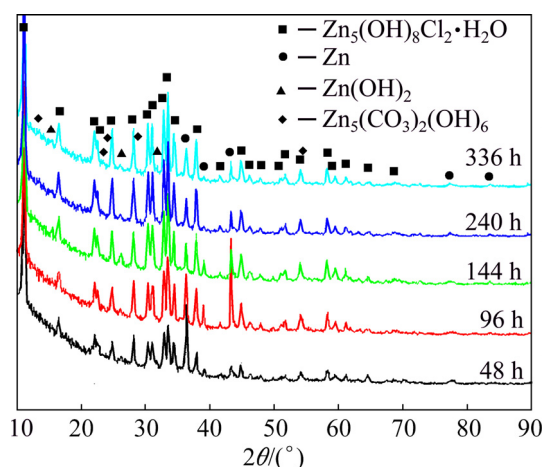


Fig. 4 X-ray diffraction patterns of zinc for different exposure time

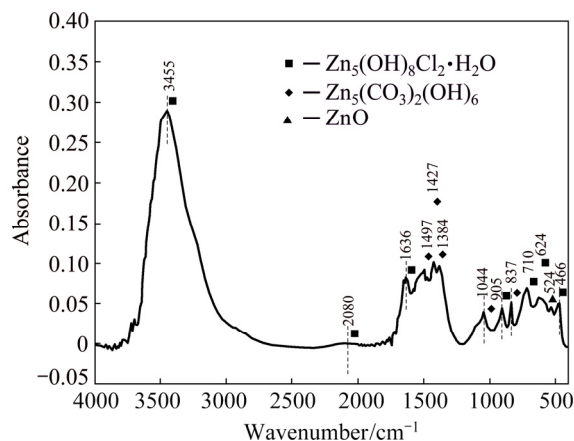


Fig. 5 FTIR results of zinc for exposure time of 336 h

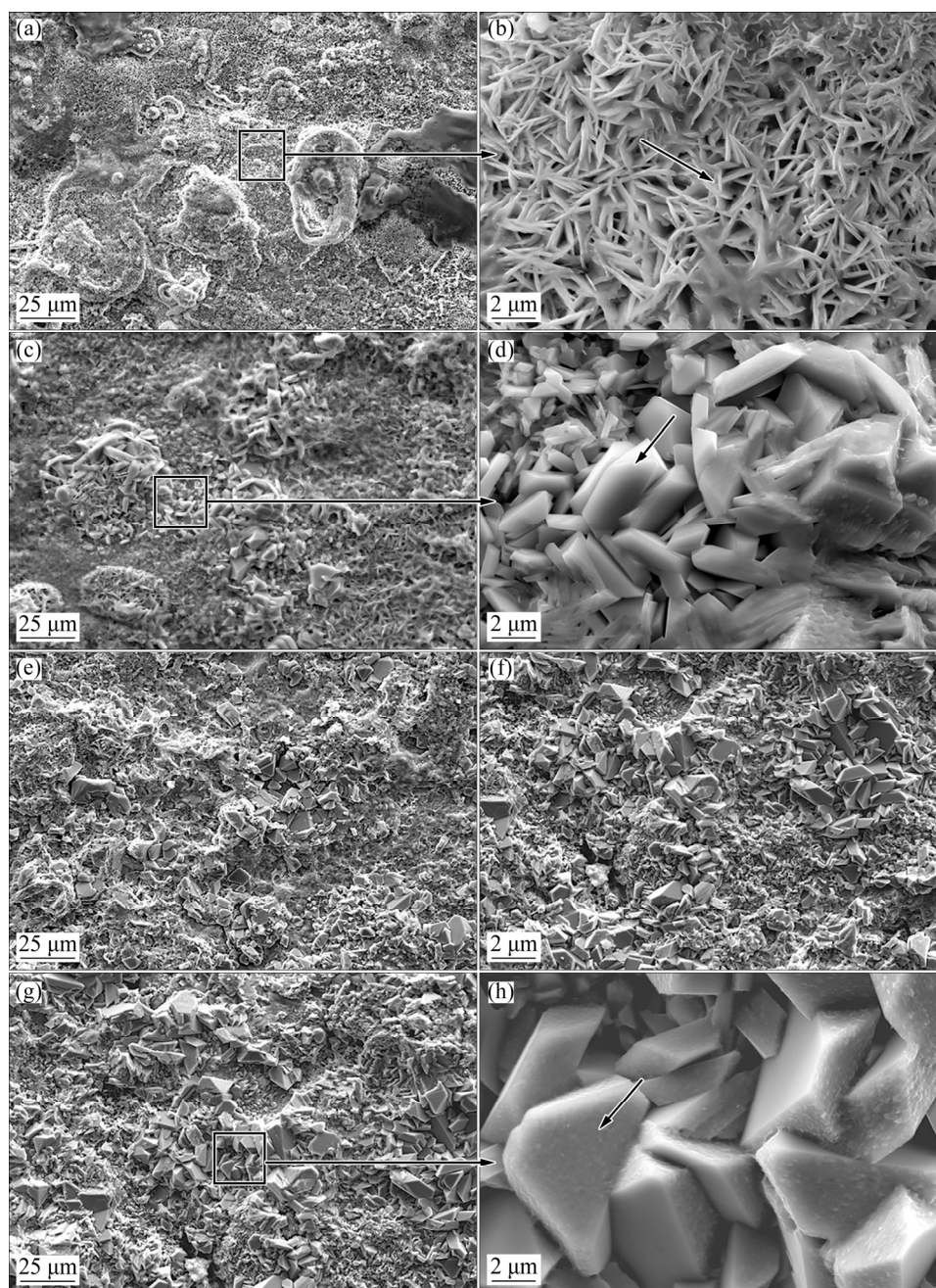


Fig. 6 SEM images of zinc for various exposure time: (a, b) 48 h; (c, d) 96 h; (e) 144 h; (f) 240 h; (g, h) 336 h

Table 1 Element contents of corrosion products marked in Fig. 6 determined by energy-dispersive spectroscopy (molar fraction, %)

Location	Zn	O	Cl	C
Fig. 6(b)	77.9	8.4	–	13.6
Fig. 6(d)	57.8	29.6	12.6	–
Fig. 6(h)	59.5	28.1	12.4	–

However, CL is a good physical barrier against the corrosive media. So, the protectiveness of the corrosion product layer in this work is more likely to be attributed to the formation of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$.

Figure 8 displays the typical corrosion morphology of the corroded samples after removing corrosion products for 336 h. Plenty of local pits are found to be distributed uniformly on the surface of zinc (Fig. 8(a)). A high magnification image of a pit shows that the pit has a polygon shape with some crystal orientations and plains (Fig. 8(b)). Furthermore, there are some evidences that the attack is along grain boundaries in some areas which are marked by arrows. These observations certify the preferential corrosion along some sensitive structures. This phenomenon was investigated by ALVAREZ and GALVELE [37] and they highlighted that zinc dissolution did not propagate in a flat front but developed

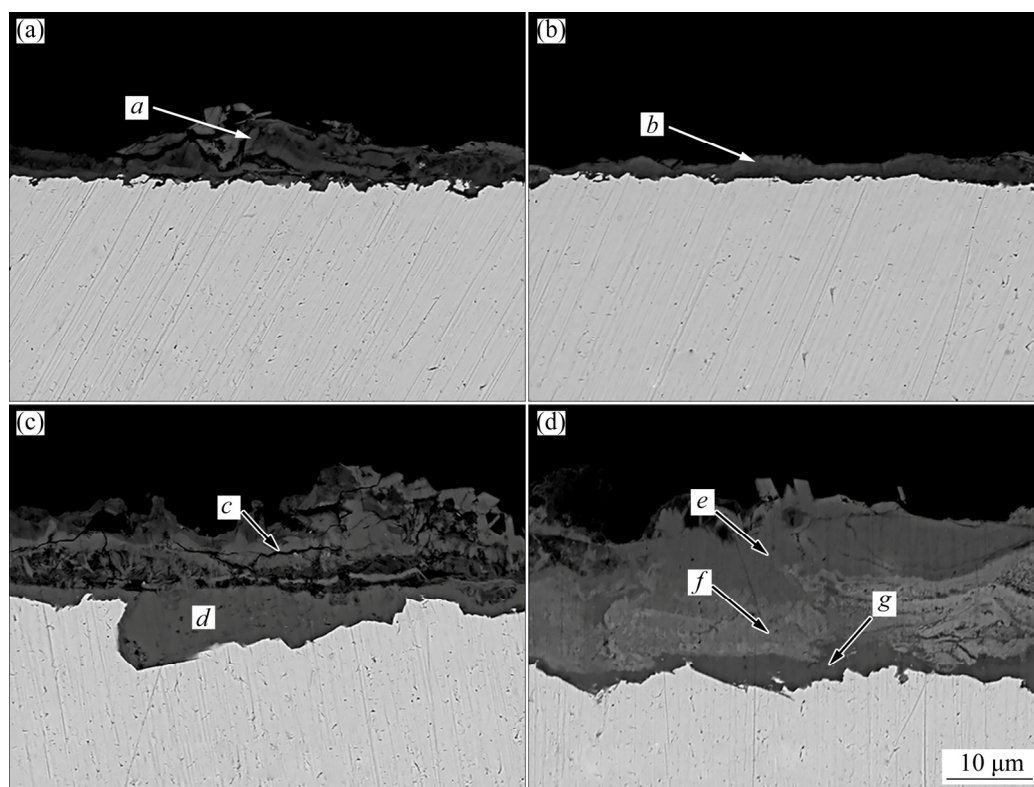


Fig. 7 Cross-sectional morphologies of zinc corrosion products at different locations for different exposure time: (a, b) 48 h; (c, d) 336 h

Table 2 Element contents of corrosion products marked in Fig. 7 determined by energy-dispersive spectroscopy (molar fraction, %)

Point	Zn	O	Cl	C
<i>a</i>	55.4	27.0	5.12	12.5
<i>b</i>	52.4	23.4	6.75	17.4
<i>c</i> (Outer layer)	49.4	30.3	3.72	16.6
<i>d</i> (Inner layer)	57.9	29.4	12.6	–
<i>e</i> (Outer layer)	46.9	24.4	9.04	19.7
<i>f</i> (Middle layer)	50.1	24.1	7.48	18.3
<i>g</i> (Inner layer)	52.9	22.4	8.72	16.0

along certain crystallographic planes. They concluded that pitting of zinc in NaCl solutions developed along $\{0001\}$ or $\{10\bar{1}0\}$ planes.

3.4 Electrochemical characteristics of corrosion product layer

The effects of corrosion product layer on corrosion behavior of zinc were further studied by the EIS technique, which could provide detailed information about the corrosion process at electrolyte/electrode interface [25,31]. Figure 9 shows the Nyquist plots and phase Bode plots for the corroded zinc and the equivalent circuit is shown in Fig. 10.

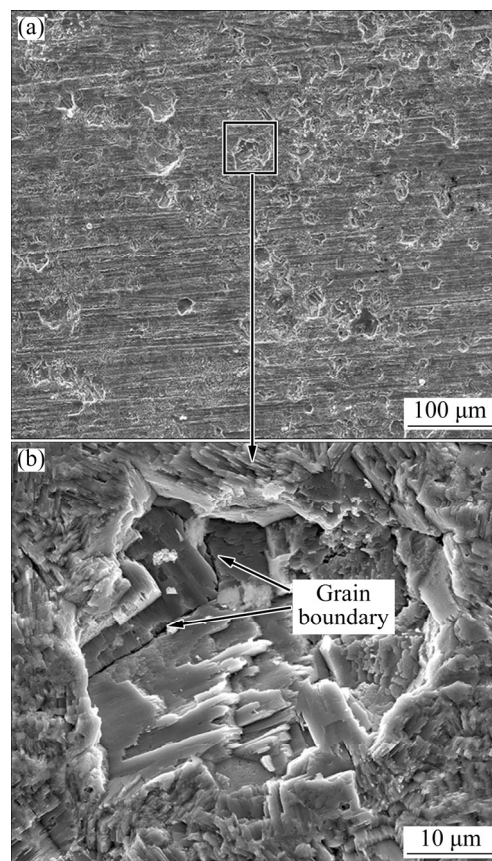


Fig. 8 Corrosion morphologies after removal of corrosion products of zinc for exposure time of 336 h

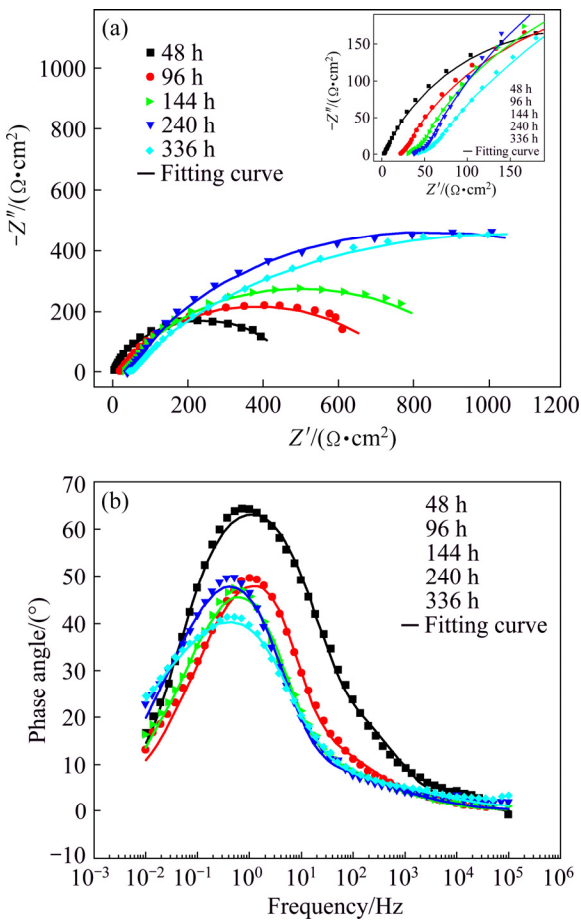


Fig. 9 Nyquist plot (a) and phase Bode plot (b) of zinc for various exposure time

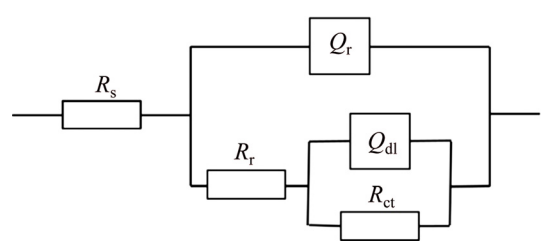


Fig. 10 Equivalent circuit

In Fig. 10, R_s is the electrolyte resistance, Q_r and R_r represent the dielectric properties of the corrosion product layer, and Q_{dl} and R_{ct} are used to describe the charge transfer process. The fitting parameters are given

Table 3 Values of parameters shown in Fig. 10

Exposure time/h	$R_s/(\Omega \cdot \text{cm}^2)$	Q_r			$R_r/(\Omega \cdot \text{cm}^2)$	Q_{dl}			$R_{ct}/(\Omega \cdot \text{cm}^2)$	Chi-squared value
		$y_r/(\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{S}^{-n})$	n_r			$y_{dl}/(\Omega^{-1} \cdot \text{cm}^{-2} \cdot \text{S}^{-n})$	n_{dl}			
48	2.03	1.14×10^{-3}	0.626	2.75		1.57×10^{-4}	1.00	475	1.44×10^{-3}	
96	20.5	1.79×10^{-3}	0.621	27.9		3.79×10^{-4}	0.977	728	8.37×10^{-4}	
144	31.7	1.57×10^{-3}	0.579	26.4		8.06×10^{-4}	0.882	950	6.52×10^{-4}	
240	36.7	1.33×10^{-3}	0.559	26.7		9.05×10^{-4}	0.858	1.67×10^3	6.57×10^{-4}	
336	40.9	1.56×10^{-3}	0.464	31.6		7.96×10^{-4}	0.775	2.09×10^3	3.83×10^{-4}	

in Table 3 and the Chi-squared values show the goodness of fit. It is well known that the polarization resistance (R_p) is inversely proportional to the corrosion rate. R_p is defined as the Faraday resistance of an electrode at a certain potential when the frequency reaches zero:

$$R_p = (Z_F)_{\omega=0} \tag{5}$$

where Z_F is the Faraday resistance and ω is the frequency.

In this test, R_p can be calculated by the following equation:

$$R_p = R_{ct} + R_r \tag{6}$$

Figure 11 shows the evolution of the reciprocal of R_p as a function of exposure time. It is obvious that the reciprocal of R_p gradually decreases with the exposure time, which is in agreement with the trend of R_{corr} calculated from the mass loss measurements.

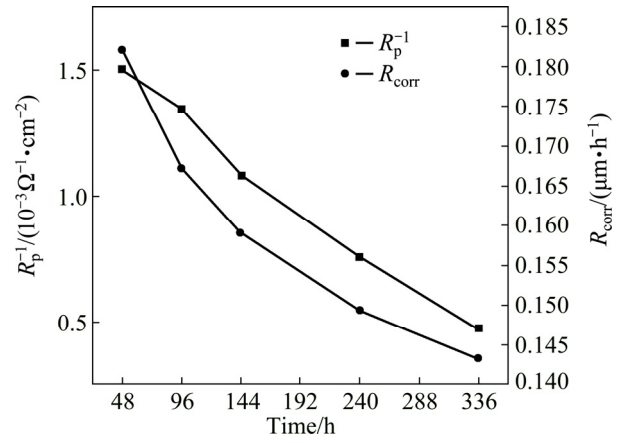


Fig. 11 Variations of R_p and R_{corr} for different exposure time

The rate-determined step (RDS) is the slowest step during the reaction process. Atmospheric corrosion generally contains three steps: (1) corrosive ions transporting to the substrate, (2) charge transfer process at the interface, and (3) corrosion products transporting to the environment. The first and last steps can be combined together as the mass transportation process. By comparing the value of R_r and R_{ct} for the same sample, the RDS of zinc atmospheric corrosion process in this

test is obtained. Table 3 gives the values of R_r and R_{ct} of samples for various exposure time. R_{ct} reflects the inhibition of charge transfer process, which is primarily due to the CL in the corrosion product layer in this test. The value of R_{ct} increases rapidly with the exposure time. It can be attributed to the gradual compacting process of the corrosion product layer, which can reduce the area of the metal/electrolyte interface. R_r reflects the inhibition of the transporting process in the corrosion product layer. It is obvious that the values of R_{ct} are about 10 times that of R_r . That is to say, the charge transfer process is the RDS throughout this test.

In the previous analysis, the CL structure is mainly due to the formation of $Zn_5(OH)_8Cl_2 \cdot H_2O$ in the corrosion product layer. So, it is reasonable to conclude that one role of $Zn_5(OH)_8Cl_2 \cdot H_2O$ in the corrosion product layer is to inhibit the charge transfer process of the atmospheric corrosion of zinc, which is the RDS in the atmosphere corrosion of zinc under tropical marine atmosphere.

3.5 Corrosion mechanism and evolution of corrosion product layer

According to the morphology of corrosion products and electrochemical analysis above, a simple schematic diagram of the zinc corrosion process under stimulated tropical marine atmosphere is proposed in Fig. 12. The serial numbers in Fig. 12(b) represent the atmospheric corrosion reactions in the following discussion.

Before zinc is exposed to the climatic test atmosphere, zinc oxide film is the first layer to form

from the reaction of zinc with oxygen. In the ambient environment containing water vapor and carbon dioxide, the hydrozincite, $Zn_5(CO_3)_2(OH)_6$, is formed instantaneously on the surface [2], which is one composition of the initial product layer (Fig. 12(a)).

In the presence of salt deposition, the water vapor can be adsorbed by the particles once the RH of the environment exceeds the deliquesced relative humidity (DRH) of the salts. As the corrosive ions penetrate into the metal/film interface, electrochemical corrosion occurs on the samples with the anodic and cathodic reactions as follows:



$Zn(OH)_2$ tends to dehydrate and is converted to zinc oxide under dry conditions:



The presence of CO_2 in the ambient atmosphere is responsible for the formation of the corrosion products of $Zn_5(CO_3)_2(OH)_6$ (Fig. 12(b)). It is supported that dissolution of CO_2 in the surface electrolytic film tends to neutralize the alkali formed in the cathodic reaction [3,12,13]:

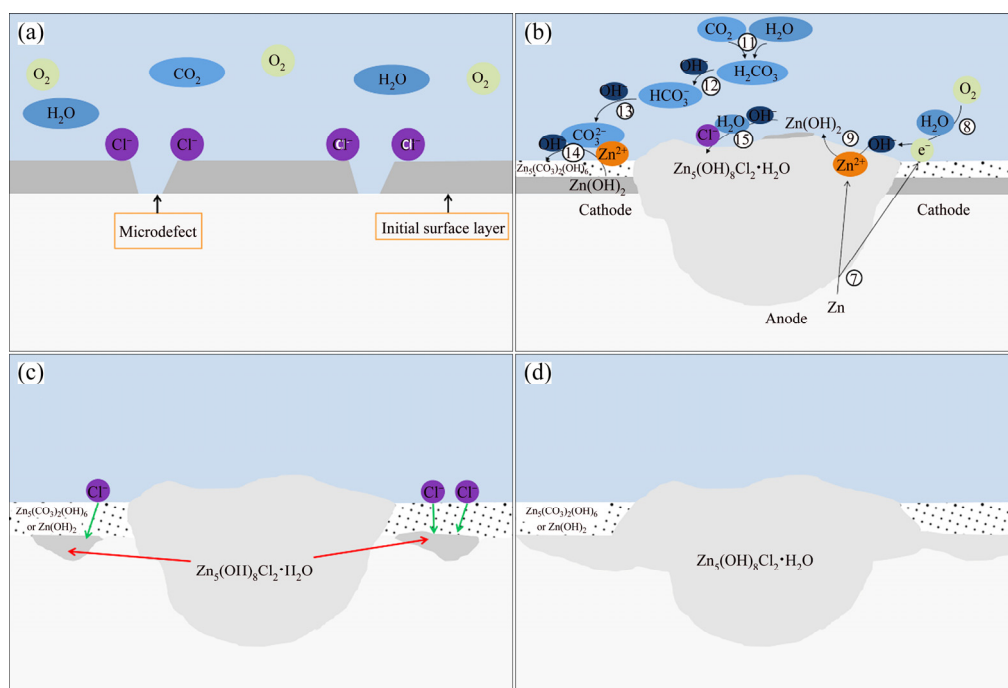
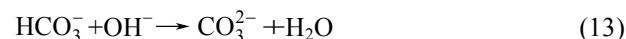
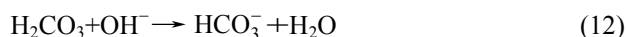
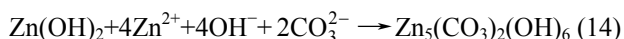
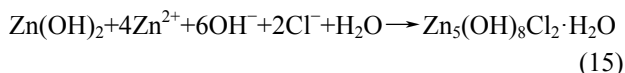


Fig. 12 Evolution schematic diagrams of zinc corrosion product layers under simulated tropical marine atmosphere condition in initial stage

Then, $\text{Zn}(\text{OH})_2$ near the cathodic region is transformed to $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$. It is assumed that one of the ubiquitous $\text{Zn}(\text{OH})_2$ molecules functions as a seed crystal and sequentially adds the needed ions from the electrolyte film [13]:



In the conditions of chlorides deposited on the surface of the zinc specimens, the chlorine ions move towards the anode sites and insoluble $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$ can be formed:



It is analyzed above that the porous $\text{Zn}(\text{OH})_2$ or $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ layer is formed on the outer layer of the corrosion product layer and the corrosive ions can easily pass through the pores. New pits are apt to be formed under that layer (Fig. 12(c)). As the exposure extends, more and more pits generate and coalesce with the neighbor pits, which results in the occurrence of double layer structures in some regions and only one compact layer in other regions (Fig. 12(d)).

4 Conclusions

1) The kinetics of the zinc atmospheric corrosion follows the empirical power law: $D = At^n$. The corrosion rate of zinc is dramatically influenced by the NaCl deposition rate, the regularity of which can be described by a power function.

2) The main corrosion products detected are simonkolleite, $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$, zinc hydroxide, $\text{Zn}(\text{OH})_2$ with trace amount of hydrozincite, $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ and zinc oxide, ZnO . The corrosion product layers have two typical structures: (1) A porous outer layer consisting mainly of $\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ or $\text{Zn}(\text{OH})_2$ and a compact inner layer primarily composed of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$; (2) Only a compact layer composed of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$. The protectiveness of the corrosion product layer formed on zinc can mainly be attributed to the compact structure composed of $\text{Zn}_5(\text{OH})_8\text{Cl}_2 \cdot \text{H}_2\text{O}$.

3) Corrosion attack in the atmospheric corrosion process of zinc is in the form of general corrosion initiated by pitting along some sensitive crystal structures.

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纯锌在模拟热带海洋大气环境下的初期腐蚀行为

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摘 要: 采用质量损失法、扫描电子显微镜–能谱法、X 射线衍射、傅里叶转换红外光谱以及电化学阻抗谱研究纯锌在模拟热带海洋大气环境下的初期腐蚀行为。动力学分析表明, 锌的腐蚀过程是一个减速过程, 且其腐蚀动力学符合幂函数经验公式: $D=At^n$ ($n<1$)。腐蚀产物中含有致密结构的碱式氯化锌, 这种结构能够阻碍锌电化学反应的控制步骤——电荷转移步骤, 从而对锌产生保护。结合形貌分析, 提出锌腐蚀产物的演化模型。此外, 锌的腐蚀速率与氯化钠沉积速率的关系可用幂函数公式描述。

关键词: 锌; 腐蚀动力学; 腐蚀产物; 电化学阻抗谱; 碱式氯化锌

(Edited by Bing YANG)