



# Article Research on Dynamic Marine Atmospheric Corrosion Behavior of AZ31 Magnesium Alloy

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**Abstract:** The dynamic marine atmospheric corrosion behavior of AZ31 magnesium alloy was investigated in situ exposed on the deck of marine scientific research vessel for 1 year. The marine scientific research vessel carried out five voyages from the coast of China to the western Pacific Ocean, while the navigation track and environmental data were collected and analyzed. The corrosion rate and characteristics were evaluated by using weight loss tests, scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and electrochemical measurements. The corrosion rate from weight loss values was  $52.23 \ \mu m \cdot y^{-1}$  after exposure for 1 year, which was several times higher than that of the static field exposure test in marine atmospheric environment of other reported literature. The main corrosion products were  $Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O$ ,  $MgCO_3 \cdot 3H_2O$  and  $Mg_2(OH)_3CI \cdot 4H_2O$ . The corrosion maybe due to the harsh corrosive environment with alternating changes in temperature and relative humidity caused by multiple longitude and latitude changes, and particularly high deposition rate of chloride during voyage, which was nearly twenty times that on the coast of China. This study provides effective data for the application of magnesium alloy in shipboard aircraft and other equipment, and provides a reference for indoor simulation experiments.

Keywords: magnesium alloy; dynamic marine atmospheric; corrosion; ocean voyage

# 1. Introduction

As the lightest structural metals, magnesium alloys possess good machinability and high thermal conductivity, which have been widely used in marine equipment, shipboard aircraft, and other fields [1–6]. However, magnesium alloys are susceptible to corrosion due to the high chemical and electrochemical activity, which limits its application, especially in corrosive atmospheric environments [7,8].

Many researchers have conducted a series of studies about the influence of environmental factors on magnesium alloys. Esmaily et al. [9] reported that atmospheric corrosion of Mg–Al alloy AM50 was strongly reduced with decreasing temperature. The research of Merino et al. [10] showed that corrosion attack of Mg and Mg–Al alloy under the salt fog test increased with increasing temperature. The relative humidity also affects the corrosion behavior of magnesium alloys significantly. The study of Lebozec et al. [11] showed that when the relative humidity increased from 75% to 95%, the corrosion rate of Mg–Al alloy AZ91D and AM50 increased accordingly. In addition to temperature and relative humidity, aggressive ions such as Cl<sup>-</sup>, accelerate the atmospheric corrosion process of magnesium alloys obviously, especially in high relative humidity environment. Jönsson et al. [12] studied the corrosion behavior of Mg–Al alloy AZ91D, which was exposed in humid air at 95% relative humidity (RH) with deposition of 70  $\mu$ g/cm<sup>2</sup> NaCl. The results showed



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**Copyright:** © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). that the corrosion attack starts at locations with higher NaCl contents. However, most research on the atmospheric corrosion process of magnesium alloys has performed tests in simulated environment [13–19] that cannot fully simulate the synergistic effect of real atmospheric environmental factors.

Recently, some further studies on atmospheric corrosion of magnesium alloys have been conducted on the basis of exposure tests in actual atmospheric environments. Jönsson et al. [20] reported that the corrosion rate of AZ91D exposed in the marine atmospheric environment of 3–5 m from Atlantic shore Brest France was 4.2  $\mu$ m/a, exposed in the rural atmospheric environment of 100 km west of Stockholm was 2.2  $\mu$ m/a, and urban atmospheric environments of Stockholm was 1.8  $\mu$ m/a. Liao et al. [21] found that the corrosion rate of AZ31B in the marine atmospheric environment (Shimizu, Japan) was much higher than that in urban areas (Osaka, Japan). These results indicated that magnesium alloys suffered more serious corrosion in the marine atmospheric environment.

There have been few studies of the corrosion behavior of magnesium alloys in dynamic marine atmospheric environment, and current research on atmospheric corrosion behavior of magnesium alloys were conducted with static field exposure test at permanent location, such as the coast or island. In contrast to static field exposure tests, marine equipment in application is mostly mobile in the ocean, and the harsh corrosive environment with high relative humidity, high deposition rate of chloride [22] and alternating changes in temperature and relative humidity caused by multiple longitude and latitude changes may affect the corrosion behavior of magnesium alloys. The corrosion behavior of magnesium alloy in the dynamic marine atmosphere environment of real ocean voyage has not been widely reported, and the dynamic marine atmospheric exposure experiment is a necessary complement to static exposure experiments and simulated atmospheric environments, and can provide effective data for the corrosion behavior research of magnesium alloys in the marine atmospheric environment.

In this work, the corrosion behavior of AZ31 magnesium alloys in the dynamic marine atmosphere during ocean voyage was studied through the atmospheric exposure experiment on the deck of *Research Vessel KEXUE*. In addition, the corrosion characteristics were evaluated by scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electrochemical measurements. This study provides effective data for the application of magnesium alloy in shipboard aircraft and other equipment.

#### 2. Materials and Methods

#### 2.1. Material Preparation

The specimen in this work was as-extruded AZ31 magnesium alloy, the extrusion temperature was 350 °C. The chemical composition was as listed in Table 1. Specimens for field exposure test were all 100 mm  $\times$  50 mm  $\times$  3 mm. All specimens were ground with 800 grit emery papers, degreased with acetone, dried with flowing air and weighed. Four replicate metal samples were retrieved from the exposure site after 1, 3, 6 and 12 months. Three replicas were used to determine weight loss of specimens, and the other one was used to analyze the corrosion morphology, corrosion products.

Table 1. The nominal chemical composition of AZ31 magnesium alloys (wt. %).

Material	Al	Zn	Mn	Si	Fe	Cu	Ni	Mg
AZ31	3.19	0.81	0.30	0.025	0.006	0.002	0.0006	Bal.

#### 2.2. Dynamic Natural Environment Exposure Test

The dynamic natural environment exposure test was carried out on the open deck of the *Research Vessel KEXUE* of the Institute of Oceanology, Chinese Academy of Sciences (Qingdao, China). As is shown in Figure 1a,b, the specimens of AZ31 magnesium alloy (as circled in red in Figure 1) were installed on the test rack with the angle of 45° horizontal to



the deck. The cumulative atmospheric exposure time was 1 year. As is shown in Figure 1c, the navigation range was around China offshore (Qingdao, China) to the western Pacific.

**Figure 1.** The dynamic natural environment exposure test environment. (**a**) Test rack A, (**b**) test rack B, (**c**) navigation range.

## 2.3. Determination Method for Natural Environmental Factors

The temperature, relative humidity (RH) and wind speed were measured by the automatic weather station of *Research Vessel KEXUE*.

The determination method for the deposition rate of chloride at the exposure test site described below was based on GJB 8894.1-2017. A double-layer medical gauze used to collect chloride ions with an area of 100 cm<sup>2</sup> was exposed at the exposure site for 7 days. Three parallel specimens of the gauze were collected each time. The collected gauze was fully cleaned, and the chloride ions concentration in the solution was measured.

### 2.4. Corrosion Rate Measurements

The corrosion rate was measured by weight loss measurements, and the corrosion products were removed by immersion in  $200 \text{ g/L CrO}_3 + 10 \text{ g/L AgNO}_3$  for 10 min at  $25 \degree$ C, and then the samples were rinsed with distilled water and alcohol, dried and weighted.

The weight loss of AZ31 magnesium after exposure for different periods was calculated by using the following equation:

$$C = (w_0 - w_1)/S$$
(1)

where *C* is the weight loss of the metal due to corrosion,  $w_0$  is the original weight,  $w_1$  is the final weighted, *S* is the surface area.

The corrosion rate of AZ31 magnesium after exposure for different periods was calculated by using the following equation:

$$v = (w_0 - w_1)/(S \cdot T \cdot \rho) \tag{2}$$

where v is the corrosion rates of the metal due to corrosion,  $w_0$  is the original weight,  $w_1$  is the final weight, S is the surface area, T is the experimental time,  $\rho$  is the density.

# 2.5. Corrosion Products Analysis

Corrosion morphology of corrosion products was observed by scanning electron microscope (Regulus 8100, HITACHI, Tokyo, Japan) and Laser confocal scanning microscopy (OLS5000, Olympus, Tokyo, Japan). Phase composition was analyzed by X-ray diffraction (Ultime IV, Rigaku, Tokyo, Japan), and the element types and valence states of the corrosion products were analyzed by X-ray photoelectron spectroscopy (ESCALAB 250Xi, Thermo, Waltham, MA, USA).

### 2.6. Electrochemical Measurements

Electrochemical measurements were performed with a electrochemical workstation (PARSTAT 4000, Princeton Applied Research, Oak Ridge, TN, USA) in 3.5% NaCl solution in a conventional three-electrode cell, where the magnesium alloy specimen was the working electrode, saturated calomel electrode was the reference electrode and Pt foil was the counter electrode. The test system was always in a steady state with no stirring. The working electrode surface was covered with silicone rubber to leave an exposed area of 1.0 cm<sup>2</sup>. Prior to testing, the working electrode was stabilized for about 30 min with open circuit potential measurement. Potentiodynamic polarization test was measured in the range of  $\pm 0.5$  V vs. the open circuit potential with the scan rate 1 mV/s. All the measurements were performed at ambient temperature ( $25 \pm 2$  °C) and repeated at least three times to maintain the reproducibility.

## 3. Results

#### 3.1. The Environment of Field Exposure

The exposure environment of the specimens is the deck of the *Research Vessel KEXUE*, which is quite different from the static field exposure test at permanent locations such as the coast or islands reported in other studies.

Firstly, the duration of navigation in the western Pacific Ocean accounted for most of exposure time. During the exposure period, the proportion of the time of dynamic state (navigation in western Pacific Ocean) was 58.1%, and static state (stopping at Qingdao) was 41.9%. The ratio of the dynamic state and static state of exposure was about 3:2, which is more consistent with the real application environment of magnesium alloys in marine equipment.

Secondly, the *Research Vessel KEXUE* went to the western Pacific Ocean to carry out a series of scientific investigations, and traveled between Qingdao and the western Pacific five times during the exposure period, experiencing large changes in temperature during four of them. During the exposure period, the average temperature in western Pacific Ocean was about 29 °C, the average relative humidity was about 78%. In Qingdao, the annual average temperature was 14.4 °C, and the lowest temperature was below 0 °C in winter. The annual average relative humidity was 75.0%. Figure 2 shows the daily average temperature and relative humidity at exposure test site during voyage. As is shown in

Figure 2, after exposure for 3 months, the *Research Vessel KEXUE* returned to Qingdao from the western Pacific Ocean with a hot and humid environment, while at that time it was winter in Qingdao, so the temperature and relative humidity of the exposure site changed significantly. A few days later, the *Research Vessel KEXUE* went to the western Pacific, and the temperature and relative humidity rose again. The changes in temperature and relative humidity in other voyages were similar. In static exposure tests, only the change in season causes the slow change of temperature and humidity, but the specimens exposed on the deck experience rapid change of temperature and humidity several times in one year. The circulation of temperature change may cause more serious corrosion [23].



**Figure 2.** Daily average temperature and relative humidity at exposure test site during voyage: (a) temperature, (b) relative humidity.

Thirdly, the specimens exposed on the deck were subjected to the severe marine environment. Table 2 shows the range and average value of environment factor during the exposure period. Figure 3 shows the proportion of different range of temperature, relative humidity, deposition rate of chloride and wind speed during the ocean voyage, according to the hourly average value. Table 3 shows the range and average value of environment factor during ocean voyage. The temperature was higher than average temperature (26 °C) for most of the time, the maximum humidity was 97%, and the maximum wind speed was above 20 m/s. It is worth noting that during ocean voyage, the deposition rate of chloride was extremely high, and was above 100 mg/m<sup>2</sup> d most of time, and the highest value was above 1100 mg/m<sup>2</sup> d. The deposition rate of chloride was much higher than the value reported in other research measured in the static marine atmospheric exposure test, as shown in Table 4.



**Figure 3.** The proportion of environment factors during ocean voyage. (**a**) Temperature, (**b**) relative humidity, (**c**) wind speed, (**d**) deposition rate of chloride.

Environment Factor	Т	RH	Cl <sup>-</sup>	Wind Speed
	(°С)	(%)	(mg/m <sup>2</sup> d)	(m/s)
Range	-0.9~33.1	18~97	63.9~1130.0	0~20.2
Average value	21.1	75.4	232.4	5.2

Table 2. The range and average value of environment factor during exposure period.

Table 3. The range and average value of environment factors during ocean voyage.

Environment Factor	Т	RH	Cl <sup>-</sup>	Wind Speed
	(°С)	(%)	(mg/m <sup>2</sup> d)	(m/s)
Range	$-0.9 \sim 33.1$	18~97	63.9~1130.0	0.2~20.2
Average value	26.0	75.7	380.4	6.8

Table 4. The deposition rate of chloride in static marine atmospheric exposure test.

Location	Climate Type	Deposition Rate of Chloride (mg/m <sup>2</sup> d)	
The Gulf of Mexico [24]	subtropical monsoon	110~311	
Zhanjiang, coastal of China [25]	subtropical monsoon	100~600	
Xisha Islands, China [22]	tropical marine climate	64.39	
Qingdao, coastal of China [26]	temperate monsoon	25	
Shimizu, coastal of Japan [21]	temperate monsoon	4.2	

It has been reported that chloride ions and relative humidity in the marine atmosphere significantly impact the corrosion processes of magnesium alloy [10,12,27]. Many studies illustrate the well-known corrosiveness of NaCl towards Mg alloys, and NaCl can form aqueous solution by absorbing water at RH > 75% [9]. As shown in Figure 3, the proportion of time when RH > 75% was 56%, which indicated that AZ31 magnesium alloy was covered by the thin electrolyte layer of high concentration of Cl<sup>-</sup> for more than half of the time during the ocean voyage. The thin electrolyte layer covering the surface of specimens provided the reaction environment for the electrochemical reaction during the corrosion process and made large areas on the surface become electrochemically connected.

Additionally, the chemical and electrochemical reactions involved in the anodic and cathodic reactions are thermally activated [28,29], and the effect of high temperature may also accelerate the anodic and cathodic reactions during ocean voyage.

Considering the synergistic effect of high temperature, high humidity, and high deposition rate of chloride, AZ31 magnesium alloy may suffer severe corrosion in hash dynamic marine exposure test compared with the static field exposure test at permanent location during ocean voyage.

## 3.2. Corrosion Rate

The weight loss of specimens exposed to the marine atmospheric environment during ocean voyage is shown in Figure 4. For the first month of the exposure period, the corrosion rate was 29.81  $\mu$ m·y<sup>-1</sup>. However, after exposure for 3 months, the slope of the curve of weight loss increased significantly. In addition, then the weight loss of specimens increased at the similar rate with the elapse of exposure time. After exposure for 1 year, the corrosion rate was 52.23  $\mu$ m·y<sup>-1</sup>, which was significantly higher compared with other static exposure studies. It was almost 3 times higher than that of the Xisha Islands [22] and 1.6 times higher than that of the Shimizu, Japan [21]. This means that AZ31 magnesium alloy suffered more serious corrosion in dynamic marine atmospheric environment.



**Figure 4.** The weight loss of AZ31 magnesium alloy in the marine atmospheric environment during ocean voyage.

Figure 5 shows the monthly average values of temperature, relative humidity and deposition of chloride ion during exposure time. It can be seen that relative humidity and the deposition of chloride ion remained at high level. In addition, at the beginning of exposure, the deposition of chloride ion increased continuously, the maximum value appeared at the time of exposure for 3 months, almost 2 times higher than that of the first month. Therefore, the corrosion rate of AZ31 magnesium alloy increased significantly after exposure for 3 months. During the following exposure period, the AZ31 magnesium alloy was covered by thin electrolyte layer of high concentration of chloride ion in most of time under the high relative humidity and high deposition of chloride ion. Therefore, the corrosion rate of specimens remained at a high level.





**Figure 5.** The monthly average values of temperature, relative humidity, and deposition of chloride ion during exposure time. (**a**) Temperature, (**b**) relative humidity and (**c**) chloride ion deposition rate.

Figure 6 shows the surface appearance of AZ31 magnesium alloy specimens with corrosion products and without corrosion products after exposure for different periods in dynamic marine environment of ocean voyage. The specimens lost their metallic luster after exposure for 1 month, and many corrosion products formed on the surface. After exposure for 12 months, the whole surface of specimens was covered by corrosion products. After removing the corrosion products, we found that the amount of corrosion pits increased, and the corrosion pits connected with each other continuously with the elapse of exposure time.



**Figure 6.** Surface appearance of AZ31 magnesium alloy specimens exposed for different periods in marine environment of ocean voyage: (**a**) with corrosion products, (**b**) without corrosion products.

Figure 7 displays the SEM of AZ31 magnesium alloy specimens exposed for different periods in the marine environment. A trace amount of corrosion products appeared on the surfaces of AZ31 magnesium alloy specimen after exposure for 1 month. After removing corrosion products, it can be seen that there were obvious corrosion pits on the surface of AZ31 magnesium alloy (as pointed by the arrow in Figure 7b). After exposure for 3 months, corrosion pits increased, and corrosion products completely covered the whole surface. After exposure for 6 months, a large number of corrosion products gathered on the surface of the specimens, part of surface of specimen appeared the detachment of corrosion products (as circled in red in Figure 7a), and corrosion pits connected with each other (as circled in red in Figure 7b). After exposure for 12 months, thick corrosion product layers covered the whole surface of specimen with cracks.





**Figure 7.** SEM images of the surface of AZ31 magnesium alloy specimens with corrosion products exposed for different periods in marine environment of ocean voyage: (**a**) with corrosion products, (**b**) without corrosion products.

Figure 8 shows SEM images of the cross-section of AZ31 magnesium alloy specimens exposed for 12 months in dynamic marine environment of ocean voyage. After exposure for 12 months, a corrosion product layer with a thickness of more than 50  $\mu$ m was formed on the surface of specimens. However, it could also be seen that there were some small cracks in corrosion product layer. The thin electrolyte layer of high concentration of Cl<sup>-</sup> might permeate into the matrix through these cracks, which might weaken the protection of corrosion products.



**Figure 8.** SEM images of the cross-section of AZ31 magnesium alloy specimens exposed for 12 months in dynamic marine environment of ocean voyage.

Figure 9 shows the laser confocal scanning microscopy (LCSM) analysis of AZ31 magnesium alloy specimens exposed for different periods in marine environment. The maximum pit depth presented a significant increase with prolonged exposure time. The maximum pit depth of specimens after exposure for 1, 3, 6 and 12 months were 44.213  $\mu$ m, 63.048  $\mu$ m, 172.344  $\mu$ m and 276.366  $\mu$ m, respectively. The research of Cui et al. [22] showed that the deepest pits of AZ31 magnesium alloy exposed on Xisha Island, with a tropical marine climate, after exposure for 1,3 and 6 months were all in the order of 30  $\pm$  3  $\mu$ m. The value of pit depth of AZ31 magnesium alloy exposed in dynamic marine atmospheric environment was significantly higher compared with other static exposure studies.



**Figure 9.** Laser confocal scanning microscopy (LCSM) of AZ31 magnesium alloy specimens without corrosion products exposed for different periods in marine environment of ocean voyage. (a) 1 month, (b) 3 months, (c) 6 months, (d) 12 months.

The analysis of the surface morphologies shows that the corrosion of AZ31 magnesium alloy was influenced by dynamic marine environment significantly. At the beginning of exposure, the corrosion products were formed at active sites under the corrosiveness of chloride ion. After exposure for 3 months, the average deposition rate of chloride ion was highest (in Figure 5). Under the synergistic effect of high temperature, high relative humidity and high deposition rate of chloride ion, a lot of corrosion products were formed on the surface of specimens after exposure for 3 months. After exposure for 6 months,

specimens experienced temperature difference caused by ocean voyage from Qingdao to the western Pacific several times. The volume changes in the matrix and the corrosion product layer was different when temperature changed rapidly. Therefore, there was obvious stress at the interface between matrix and the corrosion product layer, which accelerated the detachment of corrosion products and the formation of cracks. The change in temperature and hash environment factor such as high wind speed and storm damaged the integrity of corrosion product layer seriously. As discussed in Section 3.1, the specimens were covered by a thin electrolyte layer of high concentration of chloride ions in most of time during ocean voyage. Therefore, the solution contained chloride ions that had stubbornly penetrated into the corrosion product layer through destroyed area of corrosion product layer, causing the amount and depth of the local corrosion to increase continually. With the extension of exposure time, more and more corrosion pits connected with each other, leading to the general corrosion and expansion of corrosion to the matrix.

#### 3.4. Corrosion Product Analysis

The composition of corrosion products can be analyzed by XRD [30]. Figure 10 shows the composition of corrosion products formed on AZ31 magnesium alloy after exposure for 12 months. The results showed that the main corrosion products generated on AZ31 magnesium alloy were carbonate-containing compounds  $Mg_5(CO_3)_4(OH)_2$ ·4H<sub>2</sub>O (JCPDS 25-0513) [31] and MgCO<sub>3</sub>·3H<sub>2</sub>O(JCPDS 70-1433) [32], and chloride-containing compound  $Mg_2(OH)_3Cl$ ·4H<sub>2</sub>O (JCPDS 07-0412) [33]. This indicates that CO<sub>2</sub> and Cl<sup>-</sup> participated in the corrosion process.



Figure 10. XRD patterns of AZ31 magnesium alloy: (a) corrosion products, (b) matrix.

Figure 11 shows the XPS spectrum of corrosion products formed on AZ31 magnesium alloy exposed for 12 months in the marine environment of ocean voyage. The element C existed as  $CO_3^{2-}$ , C-O, C=O and C-H or C-O, and carbon-containing pollutants existed on the surface of specimens. The element O existed as  $CO_3^{2-}$  and OH<sup>-</sup>. The ratio of  $CO_3^{2-}$  and OH<sup>-</sup> in the corrosion products was about 5.5:1, which indicated that  $CO_2$  participated in the corrosion reaction process in the hot and humid environment and there were a large amount of  $CO_3^{2-}$  containing compounds in the corrosion products. This was consistent with the results of XRD. As shown in Table 5, the proportion of Cl 2p was 12.69%. Combined with the previous analysis of XRD and the high deposition rate of chloride, the Cl 2p in the whole-range spectra was due to chlorine-containing corrosion products and the deposition of chloride ions.



**Figure 11.** The XPS binding energy spectrum of corrosion products formed on AZ31 magnesium alloy exposed for 12 months in the marine environment of ocean voyage: (**a**) narrow scan spectrum of C 1s, (**b**) narrow scan spectrum of O 1s, (**c**) whole spectrum, (**d**) proportion of the different states of element O.

**Table 5.** The XPS analysis of the corrosion products formed on AZ31 magnesium alloy exposed for 12 months.

Element	S 2p	Cl 2p	C 1s	O 1s	Mg 2p	Zn 2p
Atomic %	1.99	12.69	29.6	41.71	13.7	0.3

# 3.5. Electrochemical Behavior Analysis

Figure 12 shows the polarization curves of AZ31 magnesium alloy matrix and after exposure for 12 months. The corrosion potential and current density are listed in Table 6. Compared with the AZ31 matrix, the specimens after exposed for 12 months showed a current density decreasing and a positive shift of corrosion potential. The current density decreased about one order of magnitude. This indicates that the corrosion products generated on the surface of specimens might impede the ion diffusion process [34]. With the

extension of exposure, more and more corrosion products were generated on surface of the specimens under the synergistic effect of high temperature, high relative humidity and the high deposition rate of chloride ion, making the plugging effect of the corrosion product layer more obvious.



**Figure 12.** The polarization curves of AZ31 magnesium alloy matrix and specimen after exposure for 12 months in marine environment of ocean voyage.

**Table 6.** The corrosion potentials ( $E_{corr}$ ) and corrosion current density ( $i_{corr}$ ) obtained from anodic polarization curves of AZ31 magnesium alloy.

Specimens	Potential (E <sub>corr</sub> /V)	Corrosion Current Density (i <sub>corr</sub> /Acm <sup>-2</sup> )
Matrix 12 months	-1.532 -1.508	$egin{array}{ll} 1.054 imes10^{-4}\ 2.984 imes10^{-5} \end{array}$

# 4. Discussion

Figure 13 shows the corrosion process schematic of AZ31 magnesium alloy during exposure in the dynamic marine atmosphere.



Figure 13. The corrosion process schematic of AZ31 magnesium alloy.

During the initial stage of the reaction, chloride ions attached to the defects on the specimen surface and reacted with magnesium substrate and magnesium corrosion products, and destroyed the integrity of the surface. The thin electrolyte layer of high chloride ion concentration covered on the surface of specimens provides the reaction environment for the electrochemical reaction and make large areas on the surface become electrochemically connected, the corrosion occurs rapidly, and corrosion products are generated on the surface.

The degradation of AZ31 magnesium alloy was dominated by the chemical reaction process including oxidation and hydration reactions at the beginning [9].

Anodic reaction:

$$Mg \rightarrow Mg^{2+} + 2e^{-}$$
(3)

Cathodic reaction:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_2$$
 (4)

With the extension of exposure time, the location of local corrosion increased,  $Cl^-$  diffused into the matrix through corrosion pits, and the anodic reaction taken place inside the magnesium alloy matrix, which induced deep pits in specimens. At the same time, cathodic reaction had taken place on the specimen surface to generate OH<sup>-</sup>, which could combine with Mg<sup>2+</sup> to form magnesium hydroxide and magnesium hydroxyl-carbonate layer.

According to the phase diagram of the system MgO /  $CO_2/H_2O$  [35], brucite reacted with  $CO_2$  to form MgCO<sub>3</sub> as follows [15]:

$$Mg(OH)_2 + CO_2 \rightarrow MgCO_3 + H_2O$$
(5)

 $CO_2$  reacted with H<sub>2</sub>O to form  $HCO_3^-$ , and then reacted with brucite [22]:

$$5Mg(OH)_2 + 4HCO_3^- + nH_2O \rightarrow Mg_5(CO_3)_4(OH)_2 \cdot 4H_2O + 4OH$$
 (6)

Brucite reacted with  $H^+$ ,  $Cl^-$  and  $H_2O$  to form  $Mg_2Cl(OH)_3$  as follows [36]:

$$2Mg(OH)_2 + H^+ + Cl^- + 3H_2O \rightarrow Mg_2Cl(OH)_3 \cdot 4H_2O$$
(7)

With the extension of exposure time, the location of local corrosion increased under the continuous action of high temperature and the thin electrolyte layer of high chloride ion concentration, the corrosion pits continuously sprout on the surface and connect with each other, the specimen evolved into general corrosion. Due to the synergistic action of the change of temperature, high wind speed and storms, corrosion products were peeled off from specimens, and all these harsh dynamic environmental factors accelerated the corrosion process.

# 5. Conclusions

The effect of the dynamic marine atmospheric environment on the corrosion process of AZ31 magnesium was investigated in this work. The results of this study are applicable to the coastal areas of China and the Pacific Ocean marine environment, and could provide effective data for the application of magnesium alloys in carrier plane during ocean voyage. The results can be summarized as follows:

- The corrosion rate of AZ31 magnesium alloy after exposure for 1 year in dynamic marine atmospheric environment ocean voyage was 52.23 μm·y<sup>-1</sup>, the maximum depth of corrosion pits was 276.366 μm, which is much higher than that of other research studied with static field exposure test at permanent location in marine environment. After exposure for 1 year, the main corrosion products were Mg<sub>5</sub>(CO<sub>3</sub>)<sub>4</sub>(OH)<sub>2</sub>·4H<sub>2</sub>O, MgCO<sub>3</sub>·3H<sub>2</sub>O and Mg<sub>2</sub>(OH)<sub>3</sub>Cl·4H<sub>2</sub>O. The corrosion was initiated from pitting corrosion and evolved into general corrosion.
- 2. The dynamic marine atmospheric environment is hash, with high temperature, high relative humidity and high deposition rate of chloride. The average temperature was 26.0 °C. The relative humidity was 75.7%, the proportion of time when RH > 75% was 56%. The average deposition rate of chloride ion was 380.4 mg/m<sup>2</sup>d.

3. The synergistic effect of high relative humidity and chloride ion plays an important role in the corrosion process of AZ31 magnesium alloy. During ocean voyage, the AZ31 magnesium alloy was covered by thin electrolyte layer of high concentration of chloride ion in most of time, which accelerated the corrosion of AZ31 magnesium alloy significantly.

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