Research Article

Atmospheric Corrosion Behavior of 2A12 Aluminum Alloy in a Tropical Marine Environment

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Atmospheric corrosion behavior of 2A12 aluminum alloy exposed to a tropical marine environment for 4 years was investigated. Weight loss of 2A12 alloy in the log-log coordinates can be well fitted with two linear segments, attributing to the evolution of the corrosion products. EIS results indicate that the corrosion product layer formed on the specimens exposed for 12 months or longer presents a good barrier effect. Corrosion morphology changes from pitting corrosion to severe intergranular corrosion with the extension of exposure time, resulting in the reduction of the mechanical properties.

1. Introduction

Due to their high strength and low density, 2xxx series aluminum alloys have been extensively used as structural materials in the aircraft and aerospace industries [1, 2]. However, they are prone to different forms of corrosion, such as pitting corrosion, intergranular corrosion, exfoliation corrosion, and even stress corrosion cracking when exposed in outdoor atmosphere especially in marine atmosphere.

Atmospheric corrosion studies have been conducted on aluminum alloys in laboratory controlled environments [3–5]. The main focus was on the effects of environmental factors, such as relative humidity (RH), chloride contents, CO₂, and SO₂. Sun et al. [4] investigated the exfoliation corrosion of extruded 2024-T4 by laboratory-accelerated test and found that exfoliation could occur when the RH was higher than 75%, and the higher the temperature or the Cl⁻ amount was, the more serious exfoliation the specimen suffered. BLÜCHER et al. [5] investigated the effect of CO₂ on the NaCl-induced atmospheric corrosion of AA 1070 aluminum and demonstrated that corrosion is about 10–20 times faster in CO₂-free humid air compared with air containing ambient levels of CO₂. However, the laboratory simulation tests are not sufficient for predicting actual service performance of aluminum alloys because of the differences in environment, and field exposure tests are needed.

Some field exposure tests have been conducted on aluminum alloys in various atmospheric environments and pitting corrosion [6–9], intergranular corrosion [7], exfoliation corrosion [4, 9], and stress corrosion cracking [7] have been detected. It has been illustrated that atmospheric corrosion is more serious for high strength aluminum alloys because of the addition of some alloy elements which can form second phases and accelerate the localized corrosion. For instance, Sun et al. [9] investigated atmospheric corrosion behavior of 2024 and 7075 aluminum alloys in urban, coastal, and industrial environments for 20 years. The results showed that exfoliation corrosion occurred on extruded 2024 and 7075 aluminum alloys in coastal and industrial atmospheres, and mechanical properties decreased greatly with the occurrence of exfoliation. Wang et al. [7] investigated the atmospheric corrosion of 2024-T3 alloy exposed to salt lake environment and found that weight loss of the alloy monotonically increased as exposure time prolonged in the first 2 years and then tended to be stable over time. Generally, the stabilization of weight loss during long-term exposure was attributed
to the formation of a layer of oxide film on the surface which could control the diffusion of the reaction species and inhibit the corrosion process [10]. The relationship between the protectiveness of corrosion products and the weight loss has been investigated by using electrochemical techniques [8, 11]. Liu et al. [8] investigated the influence of native oxide and corrosion products on atmospheric corrosion of pure Al through electrochemical impedance spectroscopy (EIS). They revealed that the structure and thickness of the native oxide and corrosion products were the main factors that influenced the atmospheric corrosion of pure Al. Vilche et al. [11] indicated that a bilayer structure formed on the surface of pure Al exposed to aggressive sites for 2 years by using EIS.

In this work, corrosion behavior of 2A12 aluminum alloy exposed in a tropical marine atmosphere for 4 years was investigated. The corrosion rate was determined by the weight loss method. The composition, structure, and protectiveness of the corrosion products were characterized with morphology analysis and EIS. The corrosion kinetics, the protectiveness of the corrosion products, and the corrosion mechanisms of this alloy in tropical marine atmosphere were discussed.

### 2. Experimental Details

#### 2.1. Materials Preparation

A sheet of 2A12 aluminum alloy was used in this work. Chemical composition of the 2A12 alloy was listed in Table I. Samples were wet-ground through successive grades of silicon carbide abrasive papers from P120 to P2000 followed by diamond finishing to 0.1 mm. Then the specimen was subjected to a scanning electron microscope (SEM, Quanta 250) to observe the distribution and compositions of the second phases. For the metallographic characterization, the polished surface was further etched using Keller’s reagent with the following composition: 1 mL hydrofluoric acid (HF), 1.5 mL hydrochloric acid (HCl), 2.5 mL nitric acid (HNO₃), and 95 mL water (H₂O). After ultrasonic cleaning in ethanol for 1 min and drying in air, the samples were taken immediately to a KEYENCE VHX2000 stereology microscope for microstructure observation. The microstructure of the 2A12 alloy was further investigated by transmission electron microscopy (TEM; Tecnai G² F20), with the work function of 300 kV. Thin foils for TEM were cut to about 500 μm by an electron discharge cutter and later ground and polished on both sides to a thickness of about 70 μm. Then the thin foils were ion-milled at room temperature in a Gatan PIPS with a small incident angle until perforation.

Figure 1 showed the optical micrograph (a) of the 2A12 aluminum alloy and the distribution (b) and composition ((c) and (d)) of the second phases. The grain size of this alloy varied between 20 and 200 μm (Figure 1(a)) with many intermetallic (IM) particles located in the substrate (white particles in Figure 1(b)). EDS results indicated that these particles were mainly composed of Al₂CuMg (Figure 1(c)) and AlCuFeMn(Si) (Figure 1(d)) which was consistent with the results of Chen et al. [12].

Figure 2 showed the TEM images of the IM particles and the grain boundary zones. Figure 2(a) was a typical rod-like particle which distributed in the grain. According to the selected area electron diffraction result and the previous studies [13, 14], this phase was the Mn-rich T (Al₁₉₂Cu₉Mn₉) dispersoid which usually formed in the ingot homogenization process and could refine the grain through the way of pinning grain boundary migration during recrystallization annealing process [14]. As shown in Figure 2(b), this phase was also found along the grain boundaries. Figure 2(c) showed an IM particle at the grain boundary, which was identified as S phase (Al₂CuMg) based on the selected area diffraction pattern. This kind of phase played an important role in the pitting corrosion and intergranular corrosion of aluminum alloys [15]. In addition, it is worthwhile to note that precipitate-free zone (PFZ) was not found in this alloy. Instead, there were some clean grain boundaries without precipitation particles as shown in Figure 2(d).

#### 2.2. Field Exposure Test

Samples with the dimension of 100 mm × 50 mm × 2.5 mm were used for field exposure test. Prior to the test, all the specimens were ground down to 800 grit paper and then degreased by acetone followed by cleaning in ethanol. All the specimens were weighed (original weight) and the surface area (S) was measured before test. Then all the specimens were installed on a test rack with an inclination angle of 45° horizontal to the sky and facing south in Xisha islands (112°20'E, 16°50'N), 100 meters from the coastline. The test duration was 4 years. Four replicate metal samples were retrieved from the exposure site after 1, 3, 6, 9, 12, 24, and 48 months. Three replicas were employed to determine the weight loss, and the remaining one was used to analyze the corrosion morphology and the corrosion products.

Table 2 lists the annual average environmental parameters and atmospheric pollutants measured at Xisha islands during the exposure, which is consistent with the description in our previous work [16]. The annual average temperature in Xisha marine atmosphere was 27°C with the maximum temperature increasing up to 33.3°C and the minimum temperature reducing to 20.1°C which was also a relatively high temperature. The extreme relative humidity (RH) values oscillated between 61% and 94% with a mean value of 77%. Time of wetness, which was defined as the period during which a metallic surface was covered by adsorptive and/or liquid film of electrolyte, was another important factor that affects the corrosion behavior of metals in atmosphere. Schindelholz et al. [17] summarized that the TOW determination methods represented in the literature and practice could be categorized by the way in which TOW was treated either as an environmental parameter or as a surface parameter. However, both of the two methods including ISO 9223 and other indirect electrode sensors had their limitations [18, 19]. In this work, the TOW was treated as an environmental parameter.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Chemical composition (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
</tr>
<tr>
<td>2A12</td>
<td>0.13</td>
</tr>
</tbody>
</table>
Figure 1: Microstructure of 2A12 aluminum alloy used in this work: (a) optical micrograph, (b) SEM images of the distribution of second phases, (c) EDS of AlCuMg particles, and (d) EDS of AlCuFeMnSi particles.

Table 2: Climatic parameters and atmospheric pollutants of Xisha islands during 4 years of exposure.

<table>
<thead>
<tr>
<th>Exposure site</th>
<th>Xisha</th>
<th>TOW</th>
<th>2562 h/year ($\tau_4$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Location</td>
<td>112°20′E, 16°50′N</td>
<td>Rainfall</td>
<td>1526 mm/year</td>
</tr>
<tr>
<td>Max. temperature</td>
<td>33.3°C</td>
<td>Cl$^-$ deposition rate</td>
<td>112.68 mg/m$^2$ d ($S_2$)</td>
</tr>
<tr>
<td>Min. temperature</td>
<td>20.1°C</td>
<td>SO$_2$ deposition rate</td>
<td>&lt;0.1 mg/m$^2$ d ($P_0$)</td>
</tr>
<tr>
<td>Average temperature</td>
<td>27°C</td>
<td>Sunshine</td>
<td>2675 h/year</td>
</tr>
<tr>
<td>Max. RH</td>
<td>94%</td>
<td>pH of rain</td>
<td>6.5</td>
</tr>
<tr>
<td>Min. RH</td>
<td>61%</td>
<td>Distance to sea</td>
<td>100 m</td>
</tr>
<tr>
<td>Average RH</td>
<td>77%</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

and was calculated according to ISO 9223, which defines TOW as the length of time when the RH is greater than 80% at a temperature above 0°C. With this method, the approximate TOW in Xisha islands was 2562 h/year which belonged to the classification of $\tau_4$ [20]. As for the corrosive species precipitated on the samples, the Cl$^-$ and SO$_2$ deposition rates were considered and measured using the method given by ISO 9225 [21]. The Cl$^-$ deposition rate was determined by the wet candle method and the SO$_2$ deposition rate was determined using alkaline surfaces of porous filter plates saturated by a solution of sodium carbonate. According to the results, the annual average deposition rate of chloride was 112.68 mg/m$^2$ d, which was classified under $S_2$ [20]. Meanwhile, the precipitation of SO$_2$ was less than 0.1 mg/m$^2$.d and the rain had a near-neutral pH of 6.5 because of the absence of heavy industry at the exposure site.

Figure 3 showed the monthly average temperature, RH, TOW, and Cl$^-$ deposition rate during the exposure test. The temperature presented a seasonal characteristic with a higher value in summer and lower value in winter (Figure 3(a)). As for the RH and TOW, the highest value all appeared at October, while the gap between other months was not so great (Figures 3(b) and 3(c)). In addition, variation of the Cl$^-$ deposition rate exhibited no trend here. It fluctuated with
the exposure time with a higher value in the second half of
one year (Figure 3(d)).

2.3. Weight Loss Measurement. Corrosion products of the
withdrawn triplicate specimens were chemically removed
by pickling in the solution (50 mL H$_3$PO$_4$ + 20 g CrO$_3$ +
1 L H$_2$O) for 10 min at 80–100°C. After that, the specimens
were rinsed with distilled water, dried in warm air, and
then weighed to obtain their final weights ($w_1$). Meanwhile,
the metal loss caused by picking was determined by using
uncorroded sample. Then, the weight loss was calculated as
follows:

$$W = \frac{w_0 - w_1}{S} - W_{un},$$

(1)

where $W$ was the weight loss of the metal due to corrosion
(g/m$^2$), $w_0$ was the original weight (g), $w_1$ was the final weight
(g), $W_{un}$ was the weight loss of a fresh specimen due to the
picking, and $S$ was the surface area (m$^2$). The average
corrosion rate of aluminum after exposure for different
periods was calculated by using the equation in [22]:

$$V_n = \frac{12 (w_n - w_{n-1})}{t_n - t_{n-1}},$$

(2)

where $V_n$ was the corrosion rate (g/m$^2$·year), $w_n$ was the
weight loss (g/m$^2$), $t$ was the exposure time (month), and $n$
was the period of exposure ($n = 1, 2, 3, 4, 5, 6,$ and 7 referred
to the sample exposed for 1, 3, 6, 9, 12, 24, and 48 months,
resp.).

2.4. Mechanical Properties Measurement. After removing the
corrosion products, the corroded tensile specimens were
machined according to the ASTM E8M specification with
25 mm gauge length and 6 mm gauge width, and the thickness
remained unchanged. Then, the tensile tests were carried out
according to ASTM E8M with a constant deformation rate
of 1 mm/min. A data logger was used to store the data in a
digital file. To get representative average values of the tensile
properties, three tensile tests have been carried out per each
test series.

2.5. Characterization of Corrosion Morphology and Corro-
sion Products. After the exposure test, the macroscopic ap-
pearances of the specimens with corrosion products were
taken by a D200 digital camera. Then, the microscopic
corrosion morphologies with and without corrosion prod-
ucts were observed by scanning electron microscope (SEM,
Figure 3: Monthly average temperature (a), RH (b), TOW (c), and Cl$^{-}$ deposition rate (d) during the exposure test.

Figure 4: Weight loss (a) and corrosion rate (b) of 2A12 aluminum alloy during exposure in Xisha marine atmosphere for 4 years.
Figure 5: Changes of the tensile strength (a) and elongation (b) of 2A12 alloy exposed for different time.

Figure 6: Surface appearances of the 2A12 aluminum alloy exposed for 1 month (a), 6 months (b), 12 months (c), 24 months (d), and 48 months (e).

Quanta 250). Element compositions of the corrosion products were analyzed by energy dispersive X-ray spectroscopy (EDS). Elemental distributions in the corrosion product layer were examined by electron probe microanalyzer (EPMA, JXA8230) with accelerating voltage of 15 kV and sample current of 0.02 μA. Before the EPMA experiment, the specimen with corrosion products was embedded in the epoxy resin. Then the specimen was mechanically ground down to 2000 grit SiC paper and polished with 1.5 μm diamond paste. The X-ray diffraction (XRD, Rigaku Dmax-rc) investigation was carried out in situ on the exposed specimens and conducted in a step scanning mode from 10° to 90° with Cu Kα radiation. After that, the data was analyzed with Jade 5.0 software.
2.6. Electrochemical Impedance Spectroscopy (EIS) Measurement. EIS measurements were performed with VMP3 electrochemical workstation in 0.1 M NaCl solution in a conventional three-electrode cell, using a platinum sheet as counter electrode and a saturated calomel electrode (SCE) as reference electrode. The test system was always in a steady state with no stirring. The whole metal sample was manually sectioned into coupons of dimensions 15 mm × 15 mm × 2.5 mm which served as working electrode. The working electrode surface was covered with silicone rubber leaving an exposed area of 1.0 cm². The impedance spectra were recorded in the frequency range between 100 kHz and 10 mHz with 10 mV amplitude peak to peak perturbing signal. The experimental data were analyzed by the commercial software ZSimpWin. All the measurements were performed at ambient temperature (25 ± 2°C) and repeated at least three times to maintain the reproducibility.

3. Results

3.1. Weight Loss and Corrosion Rate. Figure 4 shows the weight loss (a) and the corrosion rate (b) of 2A12 aluminum alloy during the 4-year exposure in Xisha marine atmosphere. An increasing trend in weight loss consisting of two different segments is observed in Figure 4(a). The weight loss increases rapidly during the initial 12 months of exposure and then the increasing rate decreases to a much lower value as the exposure time prolonged. Corrosion rate of the alloy decreases remarkably at the initial six months of exposure and then presents a slight augment from 6 months to 9 months. With further increasing of the weathering test, corrosion rate decreases gradually and stabilizes to a certain value. Corrosivity of aluminum alloys in atmospheric environment has been classified into five grades in some literatures [3, 9, 23] according to ISO 9223. The corrosion rate of 2A12 alloy after exposure in Xisha islands for 1 year is 34.49 g/m²·year, so it belongs to the classification of C5 (very high) based on ISO 9223 [20].

3.2. Loss in Mechanical Properties. Changes of the tensile strength and elongation for 2A12 alloy versus exposure time in Xisha marine atmosphere are shown in Figure 5. The tensile strength decreases gradually as the exposure test extends (Figure 5(a)). The biggest loss is about 40 MPa and 7.6% in percentage. As for the elongation, it reduces from 17% for the uncorroded specimen to 7.3% for the specimen exposed for 48 months. That is, the toughness loss reaches 57% in the end of the exposure test. The reduction in mechanical properties has been reported by many literatures [24, 25]. This reduction can be attributed either to hydrogen embrittlement or to the stress concentration of the corrosion-induced intergranular cracks [24].

3.3. Macroscopic Appearances. Figure 6 shows the macroscopic appearances of the 2A12 specimens exposed for different time. The surfaces are covered with corrosion products so that the original appearances of the samples cannot be seen. It is seen that the specimens become grey with increasing of the exposure time and the corrosion product layers are relatively uniform.
3.4. Corrosion Product Analysis

3.4.1. Surface Morphology. Figure 7 shows the surface morphologies of the corrosion products formed on 2A12 aluminum alloy after exposure for different time. The images demonstrate that many microcracks exist in the corrosion products which are mainly attributed to the dehydration process during the wet-dry cycles [22]. The chemical compositions of the points a, b, c, and d marked in Figure 7 are listed in Table 3. The primary elements included in the corrosion products are Al and O, with a trace amount of Mg, Na, Cl, and Ca, which mainly come from the salt particles that deposited on the surface of the metal.

3.4.2. Cross-Sectional Morphology. Cross-sectional morphologies of the corrosion product layer on 2A12 aluminum alloy after exposure for different time are shown in Figure 8. It can be seen that intergranular corrosion occurs on the specimen after only 1 month of exposure (Figure 8(a)). As the weathering time prolonged, the intergranular corrosion

Table 3: Element contents of corrosion products marked in Figure 4 determined by EDS.

<table>
<thead>
<tr>
<th>Point</th>
<th>O</th>
<th>Al</th>
<th>Mg</th>
<th>Na</th>
<th>Cl</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>67.21</td>
<td>27.84</td>
<td>1.21</td>
<td>0.98</td>
<td>1.16</td>
<td>1.60</td>
</tr>
<tr>
<td>b</td>
<td>22.73</td>
<td>75.35</td>
<td>1.92</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>c</td>
<td>65.49</td>
<td>34.51</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>d</td>
<td>64.23</td>
<td>34.71</td>
<td>1.07</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Figure 8: Cross-sectional morphology of 2A12 aluminum alloy after exposure for 1 month (a), 6 months (b), 12 months (c), 24 months (d), and 48 months (e).
crack width increases. After exposure for 48 months, the specimen surface is covered by a compact and thick corrosion product layer under which there exist some isolated pits. To determine the distribution of the elements on the corrosion products of 2A12 aluminum alloy, the EPMA map scanning analysis is performed and shown in Figure 9. It can be seen that corrosion products are mainly composed of Al and O and the chloride is mainly present along the cracks. It can be attributed that the surface AlCl$_3$ has dissolved away during the water polishing, while some AlCl$_3$ remains inside the cracks.

3.4.3. XRD Analysis. Figure 10 shows the XRD patterns of the corrosion products on the surface of 2A12 alloy after exposure for different time. It is seen that only Al(OH)$_3$ is detected in the corrosion products during the initial three months of exposure. As the exposure test increases up to 6 months, two emerging diffraction peaks around $2\theta = 18^\circ$ and $2\theta = 20^\circ$, which are identified to be Al(OH)$_3$, are detected.

3.5. EIS Measurements. EIS is an efficient method to study the surface condition of metals and also a powerful tool for evaluating the protectiveness of the corrosion product layer formed on metals [8, 22, 26]. Figure 11 shows the time variation in EIS diagrams of the 2A12 aluminum alloy before and after exposure for 1, 6, 12, and 24 months. It is seen that all impedance spectra of the specimens consist of two capacitive loops except for that of the sample exposed for 1 month as shown in Figure 11(b). It shows that a low-frequency diffusion tail appears after immersing in the 0.1 M NaCl solution for 24 h and 48 h. This is because the surface corrosion product layer on the specimen exposed for 1 month will be destroyed after immersing in the NaCl solution for a long time. Meanwhile, the intergranular corrosion crack fronts will be activated due to the permeation of the reactant species like H$_2$O and O$_2$. Once the corrosion fronts are reactivated, there is need for abundant reactant species to support the reactions. Therefore, the diffusion tail appears because the reactant species are not sufficient to sustain the corrosion reactions under the corrosion products. For the
specimens exposed for 6 months or longer, the corrosion reactions under the surface layers are slow due to the thick corrosion product films. Therefore, the diffusion is not the rate controlling step and the diffusion tail does not appear.

The equivalent circuit models in Figure 12 are used to fit the EIS results in Figure 11. Among them, Model A is used to fit the spectra with two capacitive loops and Model B is used for modeling the spectra with a diffusion tail in Figure 11(b). In Model A, \( R_p \) is solution resistance; \( Q_f \) and \( R_f \) are the constant phase element of the corrosion product layer and its resistance for the corroded 2A12 and the constant phase element of the oxide film and its resistance for the freshly prepared 2A12 samples. CPE_{dl} and \( R_e \) are the double layer capacitance and the charge transfer resistance, respectively. In Model B, the redundant \( W \) is the Warburg impedance which is associated with the diffusion process through the corrosion product layer. The fitting results are also shown as solid lines in Figure 11, which match the experimental data well, indicating that the equivalent circuits in Figure 12 are suitable for fitting the EIS results.

The polarization resistance, \( R_p \), the reciprocal of which is proportional to the corrosion rate [22], can be calculated from the two equivalent circuits as follows: \( R_p = R_f + R_e \). The \( R_p \) values of 2A12 alloy before and after exposure varying with immersion time are shown in Figure 13. It is seen that the \( R_p \) values of all the corroded specimens are higher than the 2A12 substrate after immersion in the NaCl solution for only 0.5 h. This is the reason why the corrosion rate decreases in the initial exposure periods. As the immersion test extends, the \( R_p \) values of the specimen exposed for 6 months fluctuate around that of the freshly prepared sample. Meanwhile, the \( R_p \) of the samples exposed for only 1 month exhibits lower values than the specimen without exposure, while for the specimens exposed for 12 months or longer, the \( R_p \) present significantly higher values as compared with the 2A12 substrate. This may explain why the weight loss increments become ignorable in the later stage of the exposure test (Figure 4(a)).

3.6. Corrosion Morphology without Corrosion Products. The surface corrosion morphologies of 2A12 alloy after removing corrosion products are shown in Figure 14. It is observed that some pits form after exposure for 1 month (Figure 14(a)). With the increase of exposure time (Figure 14(b)), deeper and wider corrosion spots are observed and the corrosion zone almost covers the whole surface. More and more grains are corroded away, leaving a rugged surface as shown in Figure 14(c).

4. Discussion

4.1. Corrosion Kinetics of 2A12 Aluminum Alloy in Tropical Marine Atmosphere. For aluminum and aluminum alloys, a number of studies have reported the development of corrosion loss with time, both for laboratory investigation [5] and field exposure test [6–7, 9]. Most of these studies have interpreted the data in terms of the well-known and widely applied power function [27]:

\[
W = At^n,
\]  

where \( A \) and \( W \) are the corrosion losses after one and \( t \) years of exposure, respectively, and \( n \) is a constant. This equation is a simplification of the mathematical result for oxygen diffusion through increasing thickness of the corrosion films. Townsend and Zoccola [28] have proposed a method to analyze corrosion data using linear regression analysis to fit a straight line on log-log plot by taking logarithm of (3):

\[
\log W = \log A + n \log t.
\]  

In this work, however, weight loss of 2A12 alloy is found to deviate from (3). This phenomenon can be easily observed in Figure 15, which reproduces the result in Figure 4(a) by plotting the weight loss against the exposure time in log-log coordinates. It is seen that the log-log plot of weight loss versus time presents two straight lines taking the 12 months of exposure as the turning point. This behavior has been reported by some researchers [29] who described this irregular corrosion behavior as in the following representative equation:

\[
W = At_1^n + t^{n_2} (t \geq t_1),
\]  

where \( t_1 \) is the length in months of the first period of slope \( n_1 \) and \( n_2 \) is the slope in the second period. The fitting results of the two linear segments are shown in Figure 15. It is found that the slope of the second segment (\( n_2 \)) is smaller than that of the initial segment (\( n_1 \)) and both of them are less than 0.5. The constant \( n \) is a significant parameter that can be considered as an indicator for the physicochemical behavior of the corrosion product layer [30]. Value of \( n \) lower than 0.5 suggests a parabolic growth of the layer by formation...
Figure 11: Nyquist diagrams for 2A12 aluminum alloy substrate (a) and specimens after exposure for 1 month (b), 6 months (c), 12 months (d), and 24 months (e) during the immersion test.
of protective corrosion products that decrease the corrosion rate by acting as a barrier to the transportation of aggressive agents. In this work, both $n_1$ and $n_2$ are less than 0.5, which indicates that a protective corrosion product layer forms on 2A12 aluminum during the exposure test. The relatively lower value of $n_2$ demonstrates that corrosion products formed on 2A12 aluminum after exposure for 12 months or longer exhibit a better protectiveness, which is certified by the EIS results in the following section.

Corrosion rate of the 2A12 aluminum alloy presents a deceleration trend with some fluctuations during the exposure test. Ma et al. [29] revealed that this special behavior only occurred in marine environment because of the effect of chloride. In our previous work [22], the depression of the semicircles with immersion time in Figure 8 might be caused by surface roughness and/or heterogeneities in the metal/electrolyte interface. Therefore, the film capacitance can be calculated from CPE parameters values ($Y_0$ and $n$) using the following expression [31]:

$$C_f = Y_0^{1/n}R_f^{(1-n)/n},$$

where $C_f$ is the film capacitance and $R_f$ is the film resistance.

4.2. Electrochemical Behavior of Corroded 2A12 Aluminum and Its Implication on the Protectiveness of Corrosion Products. EIS is an effective method to investigate the corrosion mechanism and evaluate the protectiveness of the corrosion product layer formed on metals. In our previous work [22], the protectiveness of the corrosion film generated on AZ31 magnesium after atmospheric exposure was investigated by immersing the corrosion product-covered specimens in NaCl solution for different time and measuring the EIS. It illustrated that EIS data of the corrod ed specimens from long time immersion is more accurate than that only from immersion for a short time. In this work, the EIS measurements are also employed to characterize the protectiveness of the corrosion products based on the calculated $R_f$ and CPE $f$ values.

The impedance of CPE is expressed as [8]

$$Z_{CPE} = Y_0^{-1}(j\omega)^{-n},$$

where $Z_{CPE}$ is the impedance of a CPE, $Y_0$ is the modulus, $j$ is the imaginary component, $\omega$ is the angular frequency, and $n$ is the power index number ($0 < n \leq 1$). CPE is commonly used to replace capacitance, but CPE is different from capacitance [8]. The film capacitance can be calculated from CPE parameters values ($Y_0$ and $n$) using the following expression [31]:

$$C_f = Y_0^{1/n}R_f^{(1-n)/n},$$

where $C_f$ is the film capacitance and $R_f$ is the film resistance. The $R_f$, $Y_0$, and $n$ values fitted from the EIS data by the equivalent circuits and the calculated $C_f$ values are listed in Table 4.

Figure 16 shows the variation of $C_f$ and $R_f$ with the immersion time. The film resistance $R_f$ represents the barrier against migration of ions in association with the corrosion reaction and is useful for estimating the protective properties of the corrosion scales [32]. A higher $R_f$ value means higher protectiveness of the corrosion scales. So it can be speculated from Figure 13 that the corrosion scales formed on the surface
Figure 14: Corrosion morphologies of specimens without corrosion products after exposure for 1 month (a), 12 months (b), and 48 months (c).

The $C_f$ value also has been used to evaluate the protective effect of the corrosion products using the parameter \[8, 32\]

$$C = \varepsilon \varepsilon_0 \frac{A}{d},$$ \hspace{1cm} (8)

where $C$ is the capacitance, $\varepsilon$ is the relative permittivity of the oxide, $\varepsilon_0$ is the vacuum permittivity, $d$ is the thickness of the product layer, and $A$ is the effective area which is highly dependent on the structure of the corrosion product layer. Loose and porous structure corresponds to a large $A$ value while dense and packed structure corresponds to a small value \[26\]. The relative permittivity of the film, $\varepsilon$, is recognized as a constant because the composition change of the corrosion products can be ignored. Figure 17 compares the $C_f$ values of the 2A12 substrate and the exposed specimens after immersion in 0.1M NaCl solution for 0.5 h. A nonmonotonous trend of $C_f$ value is observed, which indicates that both $A$ and $d$ vary during the exposure test. For the freshly prepared sample, the $C_f$ is about one order greater in magnitude than the corrosion product covered samples, ascribed to the thin film formed during the short-term immersion. After exposure for 1 month, pitting corrosion occurs and corrosion products form on the specimen, which results in the decrease of the effective area $A$ and the increase of the thickness $d$. Therefore, $C_f$ drops sharply to a low value. With increasing of the exposure time, corrosion product layer covers the whole surface that gives rise to an increase of the effective area $A$. This is responsible for the large $C_f$ of the specimen exposed for 6 months. As the exposure continues, corrosion products become denser and compact.
accompanied with the growth of the thickness, resulting in the decrease of $A$ and $d$ and consequently the decrease of $C_f$.

As the immersion test extends, the corrosion product layer is destroyed by the aggressive chloride ions and thus the $C_f$ value varies (Figure 16(b)). The $C_f$ values present an increase trend with the prolonged immersion time, indicating the reduction of the layer thickness and the enlargement of the surface area. Moreover, the $C_f$ of the specimen after 12- and 24-month exposure always keep lower values throughout the immersion test. These results once again certify the better protectiveness of the product layer generated after exposure for 12 and 24 months.

### 4.3. Localized Corrosion Behavior of 2A12 Aluminum Alloy in Tropical Marine Atmosphere

#### 4.3.1. Pitting Corrosion of 2A12 Aluminum Alloy

Due to the high content of chloride ions existing in Xisha marine atmosphere, pitting of aluminum alloys is thus highly expected. When exposed to the Xisha marine atmosphere, an oxide layer composed of alumina ($\text{Al}_2\text{O}_3$) and boehmite ($\gamma$-AlOOH) or bayerite ($\text{Al(OH)}_3$) [6] forms on the surface of the 2A12 aluminum alloy. However, there exist many intermetallic (IM) particles, such as S-phase, $\theta$-phase, and AlCuFeMn phase in the alloy (Figures 1 and 2). Because of the presence of the IM particles, some flaws occur in the oxide surrounding the IM particles which are preferentially attacked by chloride ions and leading to the initiation of pitting corrosion. The galvanic coupling effect between the IM particles and the surrounding matrix promotes the growth of the pits.

#### 4.3.2. Intergranular Corrosion of 2A12 Aluminum Alloy

IGC (intergranular corrosion) is detected on the 2A12 aluminum alloy during exposure in Xisha atmosphere. It is recognized that IGC is caused by the formation of a microgalvanic cell between the grain matrix and the grain boundary region, which includes the grain boundary precipitates and the precipitate-free zone. In this work, no obvious PFZ is detected in 2A12 aluminum alloy by TEM. Therefore, the grain boundary precipitates shown in Figure 2 are mainly responsible for the IGC propagation. According to Buchheit

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**Table 4: Values of the parameters $Y_0$, $R_f$, and $n$ as well as the calculated $C_f$.**

<table>
<thead>
<tr>
<th>Specimens</th>
<th>Immersion time</th>
<th>$Y_0$ ($F\cdot\text{cm}^{-2} \cdot \text{s}^{-1}$)</th>
<th>$n$</th>
<th>$R_f$ (Ω·cm$^2$)</th>
<th>$C_f$ (F·cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Substrate</td>
<td>0.5 h</td>
<td>$1.43 \times 10^{-4}$</td>
<td>0.846</td>
<td>4142</td>
<td>$1.30 \times 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>1 month</td>
<td>$3.1 \times 10^{-6}$</td>
<td>0.772</td>
<td>3600</td>
<td>$8.22 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>6 months</td>
<td>$1.17 \times 10^{-5}$</td>
<td>0.689</td>
<td>7369</td>
<td>$3.87 \times 10^{-6}$</td>
</tr>
<tr>
<td></td>
<td>12 months</td>
<td>$6.9 \times 10^{-6}$</td>
<td>0.579</td>
<td>29280</td>
<td>$2.15 \times 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>24 months</td>
<td>$3.7 \times 10^{-6}$</td>
<td>0.571</td>
<td>13400</td>
<td>$3.89 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

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**Figure 16(b):** The $C_f$ value varies. The $C_f$ values present an increase trend with the prolonged immersion time, indicating the reduction of the layer thickness and the enlargement of the surface area. Moreover, the $C_f$ of the specimen after 12- and 24-month exposure always keep lower values throughout the immersion test. These results once again certify the better protectiveness of the product layer generated after exposure for 12 and 24 months.
Figure 16: Fitting results of film resistance $R_f$ (a) and the calculated capacity $C_f$ (b) of the corrosion product layer during immersion test.

Figure 17: The calculated capacity $C_f$ of the corrosion products after immersion in 0.1 M NaCl for 0.5 h.

5. Conclusion

Corrosion behavior of 2A12 aluminum alloy in a tropical marine atmosphere was investigated in this work. The main conclusions were made as follows:

1. The weight loss of 2A12 aluminum alloy exposed to the tropical marine environment deviates from the well-known bilogarithmic equation $W = A t^n$.

2. The weight loss versus exposure time plot presents two segments, taking the 12 months as turning point. The slope of the second segment is significantly lower than that of the first segment, which is attributed to the good protectiveness of the corrosion product layer.

3. Mechanical properties of the 2A12 alloy decrease heavily as the exposure time extends.

4. The protectiveness of corrosion products formed on 2A12 aluminum after atmospheric exposure varies with the exposure time. Corrosion products formed after exposing for 12 and 24 months present better barrier effect against further attacks.

5. Pitting corrosion and intergranular corrosion occur on 2A12 aluminum alloy in this tropical marine atmosphere, resulting in the deterioration of the mechanical properties during the exposure.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.
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