

Article

Impact of Corrosion on the Degradation of the Mechanical Properties of 2195 and 2297 Al Alloys in the Marine Environment

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Abstract: The objective of this work was to study the corrosion behavior of 2xxx aluminum alloys in the marine environment and the degradation of mechanical properties caused by corrosion as well as to provide support for the lightweight design of marine equipment. The corrosion characteristics of 2297-T8 and 2195-T8 were observed by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) at 3, 6, 9, and 12 months of exposure, and the mechanical properties were obtained via uniaxial tensile testing. The results of the study showed the following: (1) With an increase in the exposure time, the corrosion products on the surface of 2297-T8 gradually increase, and the corrosion products on the surface of 2195-T8 accumulate rapidly. (2) The results of EDS show that the corrosion products of 2297 are mainly Al oxides and that those of 2195 are composed of Al, Fe, Mn, Si, etc. (3) Through the corrosion pit diameter, corrosion pit depth, and corrosion mass reduction rate surface, the trend of an increasing average radius of the corrosion pits and the corrosion mass reduction rate surface varies linearly, and the average depth of the corrosion pits increases dramatically after 9 months of exposure time. (4) According to the mechanical properties of the study surface, in a marine atmosphere, the degradation of 2297-T8 ductility is higher than that of 2195-T8, while the degradation of the yield stress is lower than that of 2195-T8.

Keywords: aluminum alloys; 2195-T8; 2297-T8; marine environment; mechanical properties

1. Introduction

The ocean is an essential field of national defense, and increasing attention is being paid to research on lightweight marine equipment and materials [1–3]. The 2xxx series aluminum alloys are the third generation of aluminum alloys. The weight of aluminum alloys can be further reduced by adding lithium, which has a lower relative density to aluminum while increasing the elasticity modulus of the alloys, making them potentially useful materials for marine environments [4,5]. The performance of aluminum–lithium alloy materials may deteriorate over time due to corrosion, which might lead to the loss of ships and other equipment when aluminum–lithium alloy materials are used in the marine environment for a long time. Therefore, conducting research on the corrosion behavior of 2xxx aluminum alloys in the marine environment and the degradation of the mechanical properties caused by corrosion is very important.

Many researchers have conducted studies on the corrosion behavior of 2xxx series aluminum alloys in the marine environment [6–9]. It was found that the corrosion behavior of aluminum–lithium alloys is influenced by their microstructural composition, such as

by the corrosion products produced by electrochemical reactions [10,11]. The intermetallic compound particles present in all aluminum alloys play an important role in corrosion. It is generally accepted that 2xxx aluminum alloys are more susceptible to localized corrosion due to the formation of primary cells between the intermetallic compound particles and the substrate or adjacent particles [12,13]. The size of different Al_2Cu particles has a very important influence on the performance of aluminum alloys in humid environments [14,15]. In addition to intermetallic compound particles, adding Li elements to 2xxx aluminum alloys will also affect their corrosion behavior [16–18]. Studies have shown that most of the T1(Al_2CuLi) phase exists in 2195Al-Li alloys exposed to 4.0% NaCl solution, and the T1 phase can be considered as a positive matrix [19]. The higher corrosion potential of Li and Al elements leads to their preferential dissolution from the T1-phase precipitates and promotes the hydrolysis of water, leading to solution acidification and corrosion propagation [20,21]. In the atmospheric environment, aluminum corrosion reactions lead to hydrogen absorption during the deformation of aluminum alloys, thus producing the formation of aluminum hydroxide on the surface of aluminum alloys, which has a very important impact on the corrosion resistance of aluminum alloys [22].

Several studies have reported the relationship between the corrosion behavior and mechanical properties of aluminum alloys by accelerated tests [23–25]. Researchers have found that the degradation of the mechanical properties of Al-Li alloys is mainly due to the size and location of the corrosion pit, which causes a hollow inside the metal material [8,26]. Zhao studied the corrosion behavior of 7A85 aluminum alloys exposed to an industrial marine atmospheric environment for five years and provided corrosion data of a 7000-series aluminum alloy in a marine atmospheric environment using the corrosion rate and the evolution of the microstructure (corrosion residues) [27]. Zhang verified the correlation between mechanical properties and corrosion behavior by observing the microstructural evolution of a 2297 Al-Li alloy [28,29].

In this paper, the corrosion behavior and degradation of the mechanical properties of two aluminum–lithium alloys, 2195-T8 and 2297-T8, are comparatively studied in a marine atmospheric environment with different exposure durations. This research contributes to the development and design of marine equipment.

2. Materials and Methods

2.1. Materials

The materials used in this paper are 2195-T8 and 2297-T8 aluminum–lithium alloys, and the chemical compositions of the two materials are shown in Table 1. The heat treatment technology was as follows: the solution temperature was maintained at 515 °C for 55 min (2297-T8) and 80 min (2195-T8); then, 3% cold deformation was applied, and then the aging temperature was maintained at 160 °C for 12 h. Heat treatment technology was provided by Zhengzhou Light Alloy Research Institute Co., Ltd., Zhengzhou, China.

Table 1. Chemical composition of 2195-T8 (wt.%) and 2297-T8 (wt.%).

Alloy	Al	Li	Cu	Ag	Fe	Mg	Zr	Mn
2195-T8 (wt.%)	Bal	1.09	3.98	0.42	0.14	0.44	0.11	-
2297-T8 (wt.%)	Bal	1.36	2.86	-	-	0.01	0.11	0.31

2.2. Exposure Test

The experiment took place at the marine environment exposure test site of the Southwest Institute of Technology and Engineering, with a distance of 150 m to the ocean. Table 2 shows the average temperature, relative humidity, and rainfall of the marine environment exposure test site. Single atmospheric precipitation pH values ranged from 7.12 to 8.32, with no acidic precipitation. The average (rainfall-weighted average) was 7.69. During the exposure test, the position of the sample was not moved, and no load was applied. The samples were arranged at a 45° angle and fixed to the ends of a test shelf to prevent

the movement of the specimens in extreme weather. The length of exposure of the test samples was one year, with five pieces of 2297 and 2195 taken as samples at 3-month intervals. Samples were then subjected to tensile testing to assess their mechanical response during field exposure. The field exposure sample was a standard tensile sample with the dimensions shown in Figure 1.

Table 2. The average temperature, relative humidity, and rainfall of the marine environment exposure test site.

Month	Average Maximum Temperature (°C)	Average Minimum Temperature (°C)	Average Humidity (%)	Rainfall (mm)
January	23	18	92	15
February	23	17	92	39
March	28	20	94	69
April	29	23	95	115
May	33	26	95	130
June	32	26	95	159
July	33	26	94	73
August	32	26	97	222
September	33	25	97	260
October	31	24	96	188
November	28	23	95	150
December	25	19	92	37

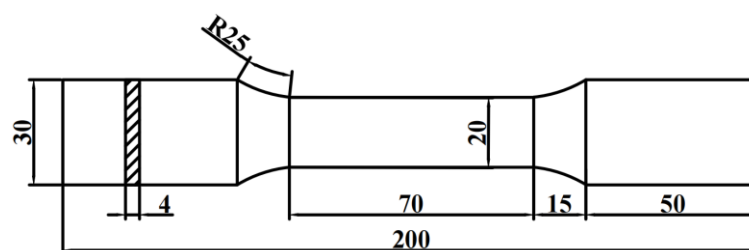


Figure 1. Standard tensile specimen geometry. The unit is mm.

2.3. Microstructural and Mechanical Characterization

In this study, SEM and EDS observations were performed with a Zeiss Sigma 300 field emission scanning electron microscope (ZEISS, Oberkochen, Germany). The working voltage was 15 KV, and the working distance was 20 mm/9 mm. SEM was used to observe the corrosion morphology before and after the corrosion products were removed. EDS was used to characterize the corrosion products. Tensile tests were conducted at room temperature using an MTS E45.105 servo-hydraulic tensile machine (Mechanical Testing & Simulation, Eden Prairie, MN, USA) with a 100 KN load cell capacity. The tensile test was carried out at a rate of 1 mm/min, and each test was carried out five times to confirm that the experimental data were accurate and repeatable. SEM coupled with EDS was used to observe the fracture surfaces after tensile testing.

3. Results and Discussion

3.1. Corrosion Behavior of Specimens

In general, corrosion products are crucial to an alloy's corrosion susceptibility during corrosion. A dense and adherent corrosion product film can effectively prevent the penetration of corrosion ions. In contrast, a ruptured and loose film of corrosion products does not provide an effective barrier. It can create diffusion channels that allow corrosion ions to reach the substrate surface and to initiate further corrosion. Figures 2 and 3 show the microstructural characteristics of 2297-T8 and 2195-T8 observed by SEM for the exposure durations of three, six, nine, and twelve months. It can be seen from Figure 2 that with the increase in exposure time, the surface corrosion of the 2297-T8 aluminum–lithium

alloy becomes increasingly severe. The residues at the grain boundaries and inside the grains also gradually increase. While there were more 2195-T8 corrosion products than 2297-T8 corrosion products, the corrosion products covered the specimen's surface at the exposure time of 3 months. It is noteworthy that the thickness of corrosion products is very uneven, which may be related to the local corrosion of the sample surface. Additionally, the corrosion products feature evident fractures, with 2297-T8 being fractured in a continuous ring due to a fracture leading to corrosion product stripping, while the fracture of 2295-T8 is dominated by intergranular fractures, with the cracks extending along the grain boundaries and peeling off from the corrosion products, as can be seen from the more in-depth corrosion morphology in Figures 2b–d and 3a–d [30]. Figure 4 shows the compositions of the corrosion products of the two alloys exposed to the marine environment for 9 months, as analyzed by EDS. From the elemental composition, we can see that the corrosion products of 2297-T8 are mainly O, Al, and C, while the corrosion products of 2295-T8 are O, Al, Mn, Si, Fe, and C. This is due to the different composition of the two alloys and also because the apertures may be related to the dry and wet cycle processes [31]. In general, the accumulation of corrosion products can partially shield the substrates. However, porous and fragmented corrosion products always facilitate the movement of corrosive ions, which causes more corrosion. Therefore, it is necessary to use other methods to further investigate the protective properties of corrosion products.

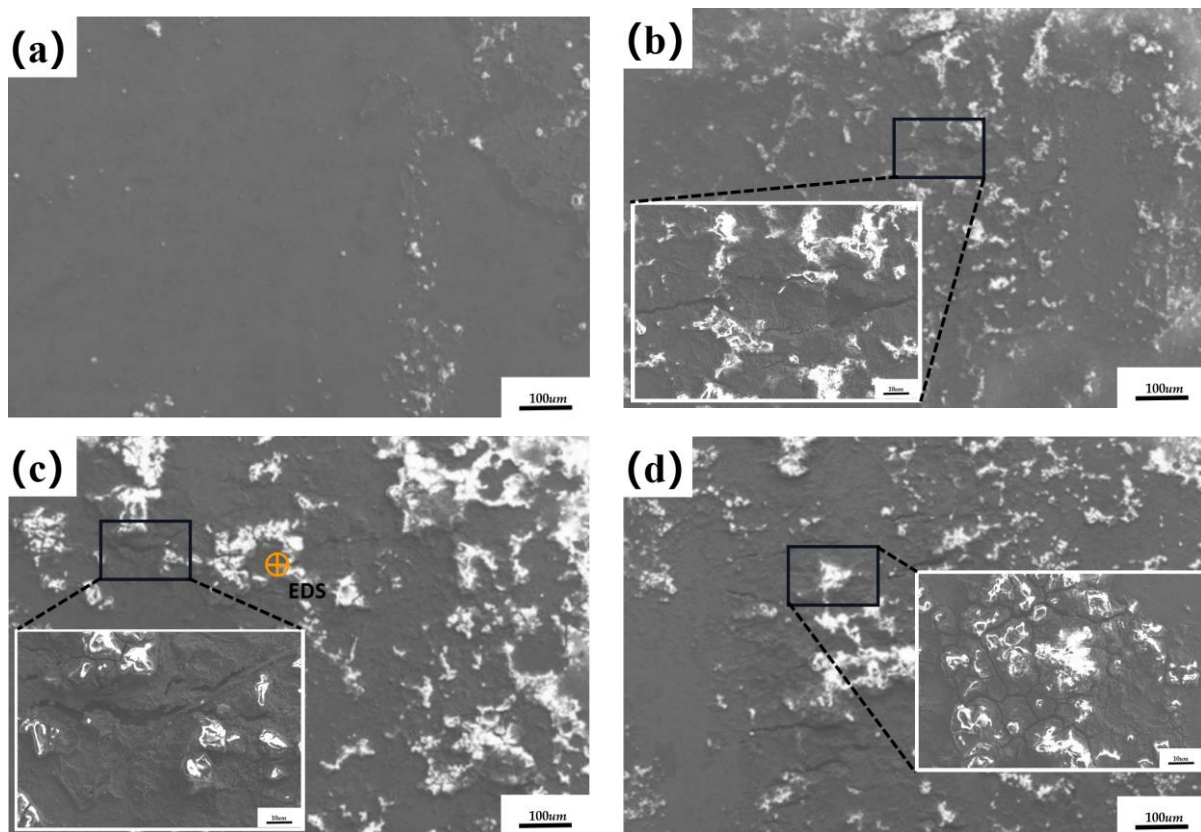


Figure 2. The microstructural characteristics of 2297-T8 observed by SEM for exposure durations of (a) three, (b) six, (c) nine, and (d) twelve months.

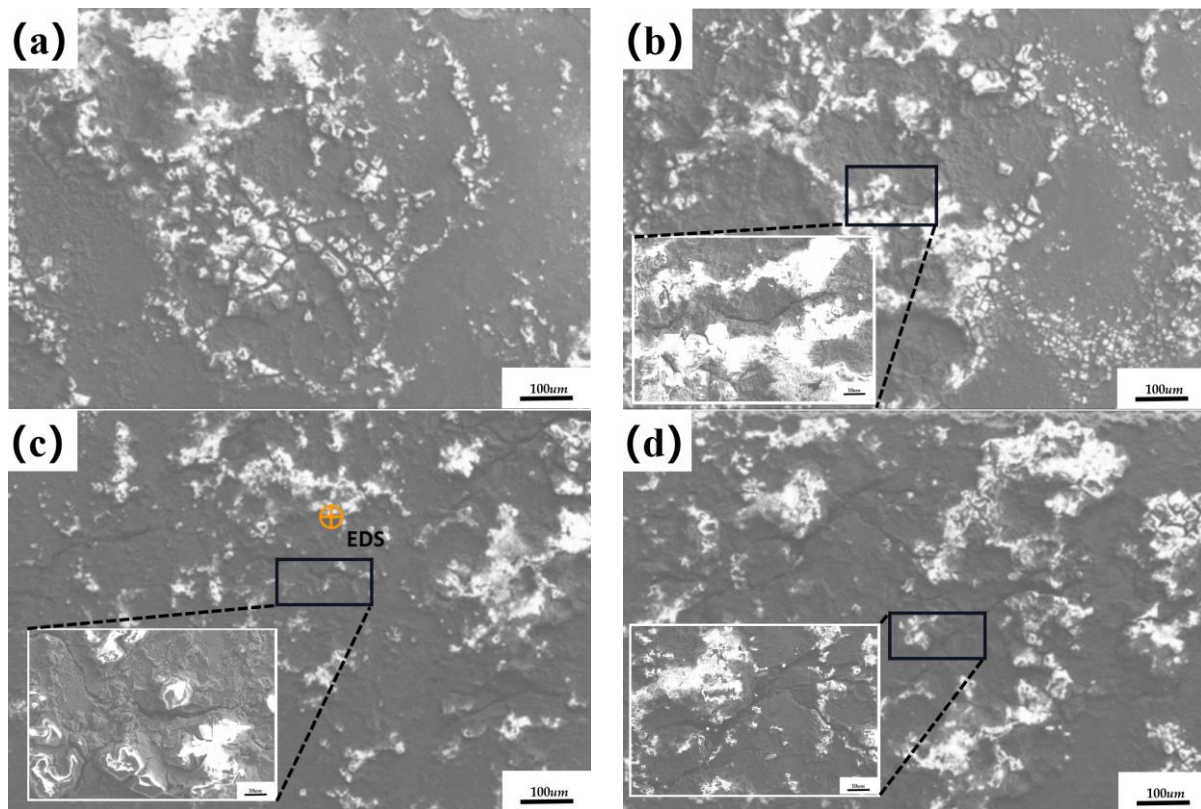


Figure 3. The microstructural characteristics of 2195-T8 observed by SEM for exposure durations of (a) three, (b) six, (c) nine, and (d) twelve months.

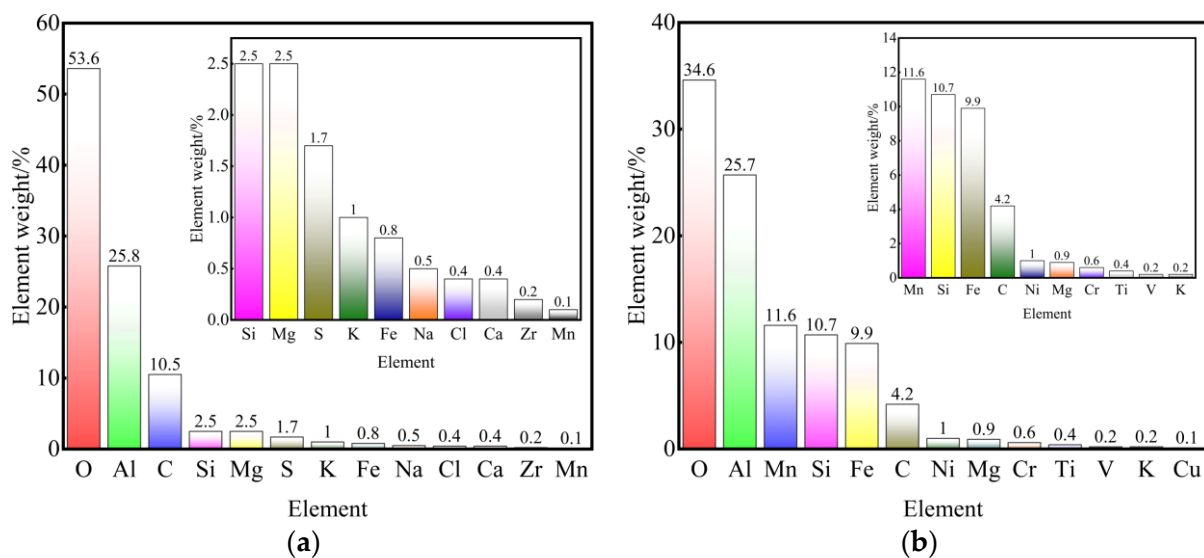


Figure 4. EDS results obtained for the regions shown in Figures 2c and 3c, of (a) 2297-T8 and (b) 2195-T8, respectively (wt%).

To further investigate the corrosion behavior of 2297 and 2195 in a marine atmospheric environment, enlarged views of the corrosion sites were observed. Figure 5 shows that the corrosion of 2297 and 2195 aluminum–lithium alloys is dominated by intergranular corrosion when exposed to a marine atmospheric environment. From the EDS results, the presence of Cu, Mg, Si, N, and O in the corrosion pits showed that after nine months of outdoor exposure, the proportion of O in 2297 and 2195 was 28.3% and 13.1%, see Figure 6. This indicates that when the substrate is corroded, the corrosion particles separate

to produce corrosion pits. Over time, the aggressive solution in the corrosion pits is diluted to form a new passivation layer. At this point, further corrosion will occur around the old corrosion pits, thus causing shallow corrosion pits to merge into larger corrosion pits.

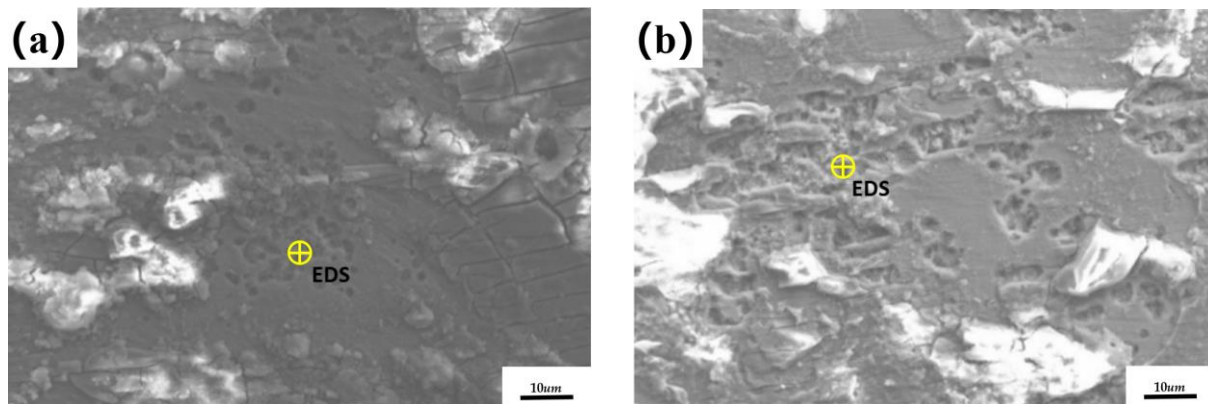


Figure 5. Microstructural characteristics of 2195-T8 (a) and 2297-T8 (b) observed by SEM for different exposure durations.

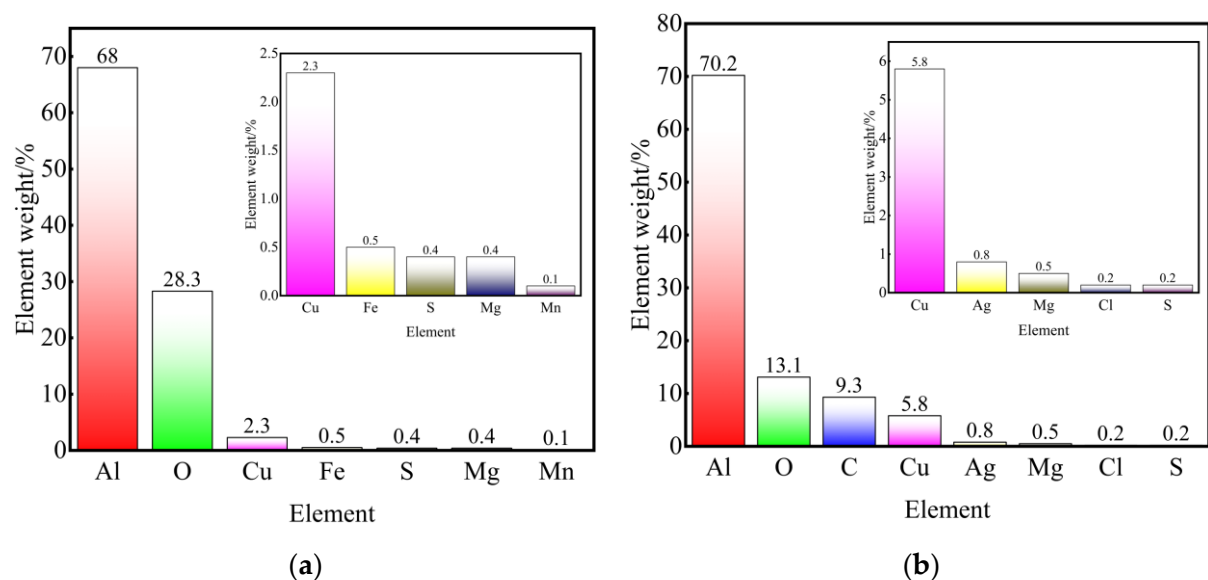


Figure 6. EDS results obtained for the regions of (a) 2297-T8 and (b) 2195-T8 shown in Figure 5a,b, respectively (wt%).

The pit diameter, which is essential in corrosion behavior, was determined. The average diameter of the corrosion pits and the average depth of the corrosion pits for the 22297 and 2195 Al-Li alloys are given in Figure 7, and the weight-loss rates for 2195 and 2297 are shown in Figure 8. Before the corrosion test, the samples first need to be cleaned using a 3% nitric acid solution in an ultrasonic cleaner at a frequency of 50 Hz. The primary purpose of the cleaned corrosion products is to avoid future effects of the corrosion product films and residual salt slurries on the testing process. The average radius of the corrosion pits for 2297-T8 with exposure times of 3, 6, 9, and 12 months was 0.02 mm, 0.06 mm, 0.11 mm, and 0.24 mm, respectively. The average radius of the corrosion pits for 2195-T8 with exposure times of 3, 6, 9, and 12 months was 0.08 mm, 0.1 mm, 0.25 mm, and 0.3 mm, respectively. The trend of an increasing average radius of the corrosion pits varied linearly, as shown in Figure 7. The average depth of corrosion pits, illustrated in Figure 7, increased dramatically after 9 months of exposure time. The decrease in corrosion rate with the exposure time is related to the accumulation of the protective layer of aluminum hydroxide. Over time, the formation of the hydroxide layer reduces the rate of aluminum

dissolution (anodic reaction). Once this reaction is complete, oxygen has no further effect on the anodic reaction.

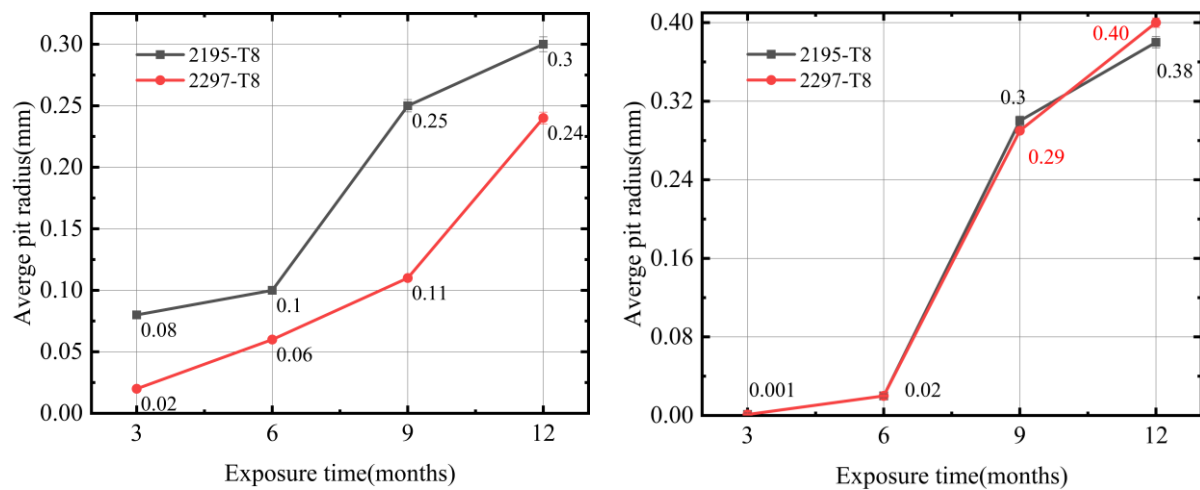


Figure 7. The average diameters of the corrosion pits and the average depth of the corrosion pits for 2297 and 2195 Al-Li alloys.

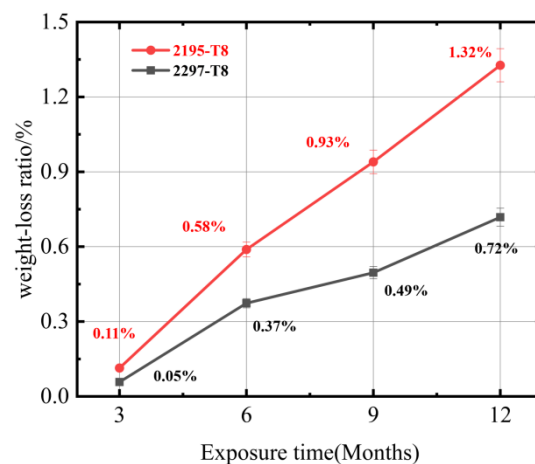


Figure 8. Weight loss rates for 2195 and 2297.

3.2. Mechanical Properties

The experimental results of the uniaxial tensile mean yield stress and mean tensile strength of the 2195-T8 and 2297-T8 specimens are given in Figure 9. The yield stress tends to decrease as the exposure time increases. It can be seen from the graph that the yield stress of 2195-T8 did not fall when the exposure time was three months, i.e., a shorter exposure time, while the decrease in the yield stress of 2297-T8 was not significant either. After 12 months of exposure time, the yield strength of 2195-T8 decreased to 88.2%, while that of 2297-T8 decreased to 78.3%. Therefore, 2195-T8 is superior to 2297-T8 in terms of yield stress reduction in a marine atmosphere.

The ductility of the two Al-Li alloys and their corrosion deterioration mechanisms were investigated. Figure 10 shows the percentage of elongation of the two aluminum–lithium alloys with different exposure times, and Figures 11 and 12 show the fracture morphology by SEM of 2297-T8 and 2195-T8 with varying exposure times, respectively. It can be seen that during the short-term corrosion time, three months, the ductility decline rates of 2297-T8 and 2195-T8 decrease. When the exposure time is six months, the ductility of 2195-T8 is still basically unchanged, while the ductility of 2297-T8 decreases to 7%. Figure 11a shows that the fracture morphology of 2297-T8 is dominated by brittle fractures and that the grain boundaries are laminar in structure. Figure 11b shows that a few dimples

appear in the section, but the fracture is still predominantly dominated by brittle fractures at this point, as shown by the orange line, which indicates the crack paths. Figure 11c shows a large number of dimples, with the main fracture form changing to a ductile fracture form. Figure 11d shows the appearance of a large ductile fracture feature caused by the stress concentration formed by the corrosion pits. The presence of other elements in 2195-T8, such as Fe, causes the fracture form of 2195-T8 to be dominated by ductile fractures after an exposure time of 3 months during the fracture process—see Figure 12a. With an increase in the exposed specimen time, a large number of corrosion products appeared on the surface of 2195-T8. Due to the presence of corrosion pits and other phases, two forms of fractures appeared on the fracture surface of 2195-T8: ductile fractures and intergranular fractures—see Figure 12b–d. This is caused by the corrosion-induced formation of surface cracks and a subsequent reduction in the adequate thickness and in hydrogen diffusion. At shorter exposure times and longer exposure times, corrosion gradually invades the specimen's surface and travels to the crystal's interior, and pores such as corrosion pits form inside the crystal, leading to the degradation of 2195-T8's and 2297-T8's properties.

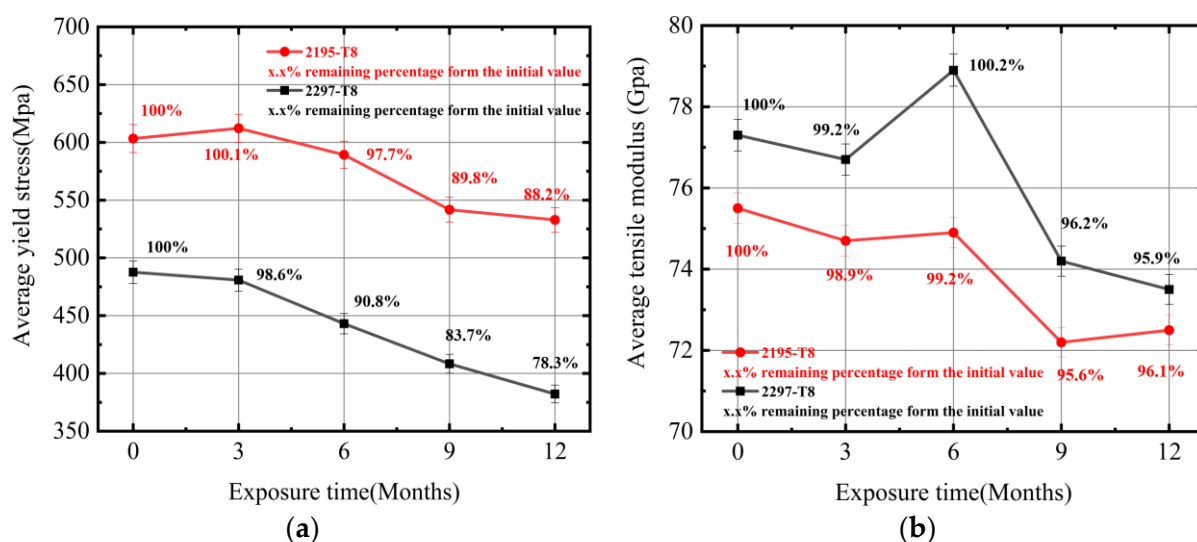


Figure 9. Experimental results of uniaxial tensile (a) mean yield stress and (b) mean tensile modulus of specimens 2195-T8 and 2297-T8.

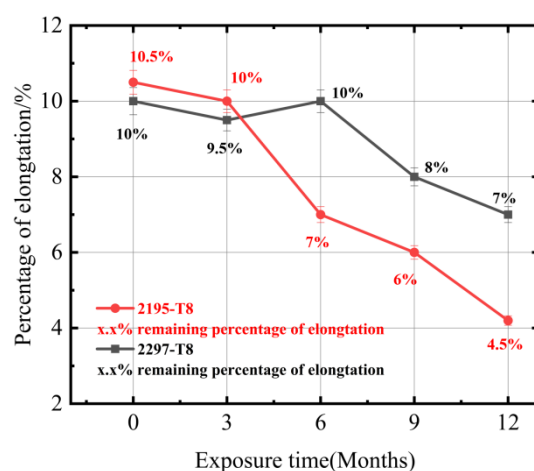


Figure 10. Percentage of elongation of the two aluminum–lithium alloys at different exposure times.

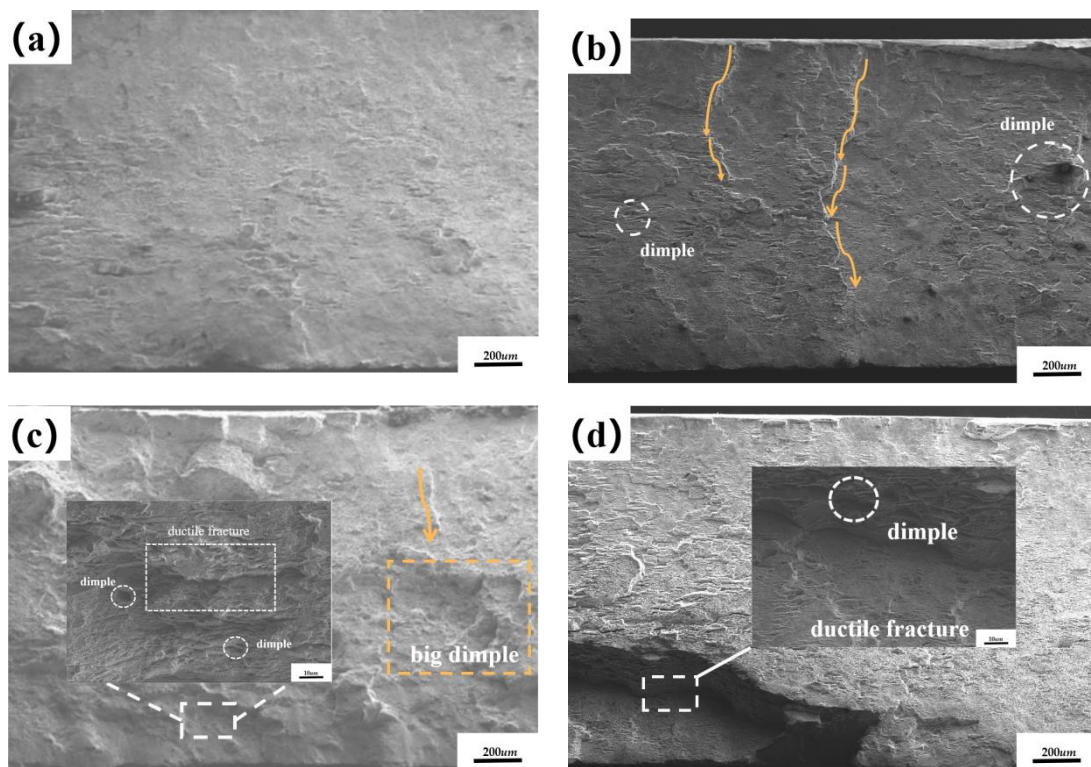


Figure 11. The fracture morphology of 2297-T8 at various exposure times. (a) 3 months; (b) 6 months; (c) 9 months; (d) 12 months.

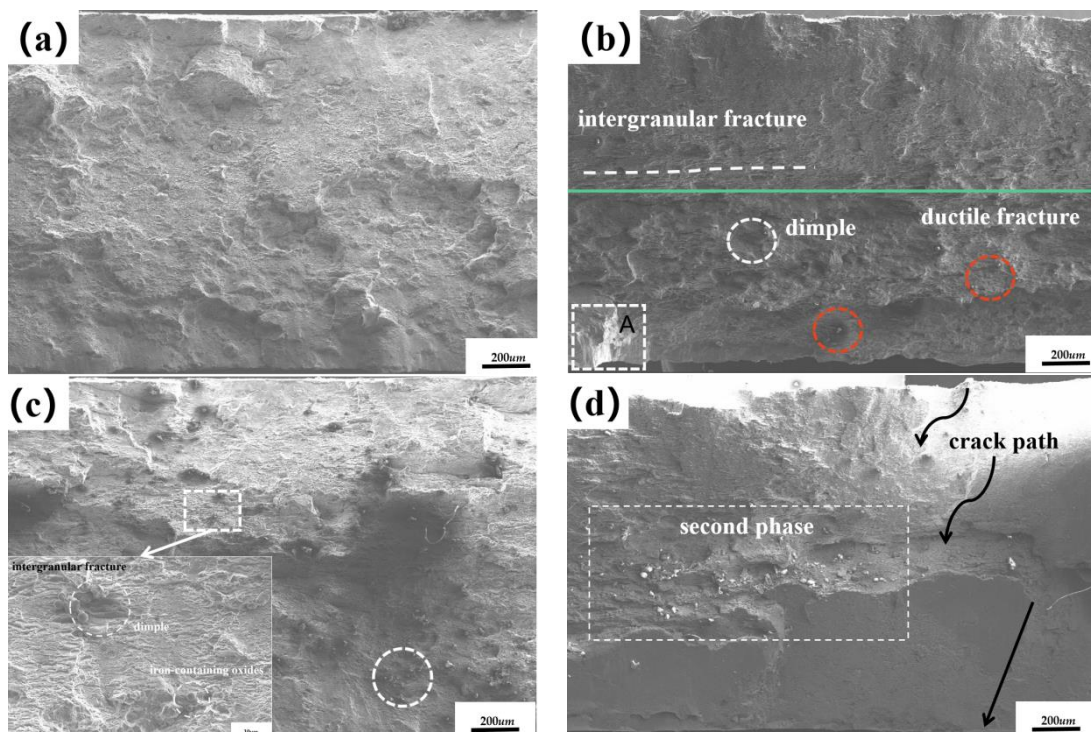


Figure 12. The fracture morphology of 2195-T8 at various exposure times. (a) 3 months; (b) 6 months; (c) 9 months; (d) 12 months.

As the exposure time increases, there is a shift from brittle fractures to ductile fractures due to the accumulation of corrosion products and corrosion pits on the surface of 2297-T8. In contrast, due to the Fe enrichment in the constituent elements, 2195-T8 will react

chemically with corrosion products to produce iron-containing oxides, which hinder the formation of tough pits and change the paths of cracks. In a marine atmosphere, the degradation of 2297-T8's ductility is higher than that of 2195-T8, while the degradation of yield stress is lower than that of 2195-T8.

4. Conclusions

In this study, the corrosion behavior and performance degradation of the aluminum–lithium alloys 2297-T8 and 2195-T8 when exposed to a marine atmosphere for 3, 6, and 9 months were investigated using SEM and EDS. The corrosion products and the cross-sectional morphology of different exposure times were observed and discussed to better understand the corrosion behavior of the aluminum–lithium alloys 2297-T8 and 2195-T8, thus promoting the application of 2xxx series aluminum alloys in a marine atmospheric environment. The following conclusions can be obtained:

- (1) With an increase in the exposure time, the corrosion products on the surface of 2297-T8 gradually accumulate, and the corrosion products on the surface of 2195-T8 accumulate rapidly.
- (2) The EDS results show that the corrosion products of 2297 are mainly Al oxides and that those of 2195 are mainly composed of Al, Fe, Mn, Si, etc.
- (3) Through the corrosion pit diameter, corrosion pit depth, and corrosion mass reduction rate surface, the trend of the increasing average radius of the corrosion pits and corrosion mass reduction rate surface varies linearly, and the average depth of the corrosion pits increases dramatically after 9 months of exposure time.
- (4) According to the mechanical properties of the study surface, in a marine atmosphere, the degradation of 2297-T8's ductility is higher than that of 2195-T8, while the degradation of the yield stress is lower than that of 2195-T8.

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Conflicts of Interest: The authors declare no conflict of interest.

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