Research Status of Corrosion Al-Li Alloy in Acid Medium

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Abstract. Aluminium-lithium alloys commonly used in aerospace at home and abroad. In this paper, Al-Li alloys are classified into four categories according to their different elements. It also summarizes its corrosion in common acidic medium, and prospects for the development and research of the next generation of new Al-Li alloys.

1. Introduction
Aluminum alloys have excellent comprehensive performance, mature design, processing methods, reliable detection, and have become the main structural materials of aerospace vehicles. In order to save fuel, improve flight speed and payload, new materials have been a hot topic of research. Lithium is the lowest density metal element in nature with a density of only 0.534g/cm³. In the aluminum alloy, for every 1% of lithium added, the density of the aluminum alloy can be reduced by 3%, and the modules of elasticity can be increased by 6% [1]. Al-Li alloys have been widely used in the aerospace industry due to their low density, high modules of elasticity, greater specific strength, low fatigue crack growth rate, and excellent low temperature performance.

2. Overview of the development of aluminium-lithium alloys
Aluminum-lithium alloys were developed in the 1920s and became a hot spot in the world in the 1980s. It has a history of nearly 100 years, and its development can be roughly divided into three stages. Therefore, the corresponding products of Al-Li alloys can be also divided into three generations [2, 3]. The first stage is a preliminary development stage, which spans from 1950s to early 1960s. The representative products are the 2020 alloy developed by Alcoa Company in the United States and the BAĐ23 alloy developed by the Soviet Union [4]. Since these first-generation Al-Li alloy products have too low plastic toughness to meet the requirements of aerospace design standards, no further applications have been made. From the 1970s to the late 1980s, it was the second stage of the development of Al-Li alloys. At this stage, a series of relatively mature products were successfully developed, including 2090, 2091, 8090 and 8091. Compared to the 2000 and 7000 series alloys, the second-generation Al-Li alloy contains 1.9-2.7% lithium, which reduces density by 10% and specificity by 25%. However, due to the anisotropy of mechanical properties, low toughness and poor corrosion resistance, Al-Li alloys are not widely used in the aerospace industry [5-8]. Since 1990s, people have reduced the lithium content to 0.75-1.8% by focusing on the above problems. At the same time, with the development of thermomechanical treatment and other technologies, the Al-Li alloys are better solved for their anisotropy, plasticity and with low toughness, some third-generation aluminum-lithium alloys with certain special advantages have been developed. Their representative products are 2097 series, 2098 series and 2099series, etc. [5, 7, 9] The table below shows the chemical composition of several Al-Li alloys.
Table 1. Chemical Compositions of Several Representative Al-Li alloys (wt.%).

| Alloy   | Cu  | Mg  | Li  | Zr  | Si  | Fe  | Others          |
|---------|-----|-----|-----|-----|-----|-----|-----------------|
| 2020    | 4.5 | -   | 1.2 | -   | 0.20| 0.30| 0.25Cd         |
| BAД23   | 4.8-5.8 | - | 0.9-1.4 | 0.11 | 0.10| 0.15| -              |
| 2090    | 2.7 | -   | 2.1 | 0.11| 0.10| 0.12| -              |
| 2091    | 2.0 | 1.3 | 2.0 | 0.11| 0.20| 0.30| -              |
| 8090    | 1.2 | 0.8 | 2.4 | 0.12| 0.10| 0.10| -              |
| 8091    | 1.9 | 0.8 | 2.6 | 0.12| 0.20| 0.30| -              |
| 2097    | 2.5-3.1 | 0.35 | 1.2-1.8 | 0.08-0.16 | 0.12 | 0.15 | 0.15Ti,0.35Zn,0.1-0.6Mn |
| 2098    | 3.2-3.8 | 0.25-0.8 | 0.8-1.3 | 0.04-0.18 | 0.12 | 0.15 | 0.10Ti,0.35Zn,0.35Mn |
| 2099    | 2.4-3.0 | 0.1-0.5 | 1.6-2.0 | 0.05-0.12 | 0.05 | 0.07 | 0.1Ti,0.4-1.0Zn,0.1-0.5Mn |

3. Corrosion of Al-Li alloys in Acidic medium

Nowadays, Al-Li alloys have been widely used in the main structure of aerospace and aeronautics to replace the traditional aluminium alloys. Al-Li alloy equipment is often in the polluted atmosphere, seawater, humid air and suffer from a certain degree of corrosion damage [10], thus affecting the strength of Al-Li alloy and the life of equipment [11-13]. Therefore, the study of the effects of different corrosion environments on Al-Li alloys is beneficial to predict the service life of equipment, so as to carry out equipment management more reasonably.

Al-Li alloys can be divided into Al-Li-Mg, Al-Li-Cu-Mg-Zr, Al-Cu-Li-Mg-Zr and Al-Li-Cu series according to their chemical composition. The following is a brief introduction to the research status of corrosion of several different Al-Li alloys in acidic media.

3.1. Corrosion of Al-Li-Mg alloy in acidic medium

LI Jin-feng et al. [14] used electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM) to study the weak acid 3.5% NaCl solution (pH=6.5) of 1420 Al-Li alloy under tensile stress of 308 MPa (close to its corresponding yield strength). The results show that, 1420 Al-Li alloy under stress-free loading has large and discrete pitting pits, as shown in Fig 1. When stress acts on 1420 Al-Li alloy, pitting pits on the surface become dense and the size decreases. Figures 2 shows the EIS plot of the 1420 aluminum-lithium alloy under stress loading. Obviously, with the increase of immersion time, two capacitive arcs appear, indicating local corrosion.

C.-X.Li et al. [15] studied the corrosion behavior of 1420 aluminum-lithium alloy in 4ml MgCl₂ droplets with an initial concentration of 0.1-1.0M at a relative humidity of 33%. Under different experimental conditions, the corrosion degree of the alloy depends on the initial concentration of MgCl₂ solution. As the relative humidity of the environment reaches equilibrium, the total effective cathode limiting current decreases with the increase of initial concentration of MgCl₂ solution. When the initial concentration of MgCl₂ droplets is 0.1M and 0.3M, the main corrosion form is filamentary corrosion. At this time, when the volt potential curve is 0.7-0.8V, there are a lot of potential transients. The form of potential transients is rapid rise and then immediately decrease, which should be related to the stop and start of filamentary corrosion. When the concentration of MgCl₂ solution increases to 1.0M, the main corrosion form is metastable pitting. At this time, more potential transients occur in the form of sudden drop and then resume, which is related to the initiation and re-passivation of metastable pits.

Figure 1. Corrosion morphology of 1420 Al-Li alloy immersed in stress-free (a) and stress (b) for 9 d
3.2. Corrosion of Al-Li-Cu-Mg-Zr alloy in acidic medium

Conde et al. [16] immersed 8090 Al-Li alloy in EXCO (4molNaCl+0.5molKNO3+0.1molHNO3, pH=0.4), and kept the temperature at 25°C, and electrochemical impedance spectroscopy was measured by electrochemical workstation. They found that with the prolongation of immersion time, the protective oxide film on the surface of the alloy basically lost. After immersion time exceeded 20 hours, the surface of the alloy would be bubbling and denuding. The longer the immersion time, the larger the bubbling and the more obvious the corrosion product film on the surface. At this time, the electrochemical impedance spectroscopy of the alloy consists of a compressed high-frequency capacitive arc and a low-frequency inductive arc. The denudation degree increases, and the two capacitive arcs are more obvious.

SU Yan et al. [17] studied the microstructure, corrosion behaviour and mechanical properties of 5A90 Al-Li alloy by using marine atmospheric environment exposure test (pH=4). The results show that Al-Li alloys are easy to enter the surface of Al-Li alloys through micro-pore of oxide film due to Cl- in the marine atmosphere, thus forming micro-corrosion batteries and causing pitting corrosion. The surface corrosion of the alloy was observed by SEM, as shown in Fig. 3. It can be found that as the exposure time of the Al-Li alloy in the marine atmosphere is longer, the corrosion layer of the surface is continuously expanded from the point to the surface to the entire surface. In the early stage of corrosion, pitting pits of different sizes are distributed on the surface of the pits, and the depth is shallow. With the extension of time, the adjacent pits connect with each other and develop vertically and horizontally, resulting in the formation of large corrosion pits.

3.3. Corrosion of Al-Cu-Li-Mg-Zr alloy in acidic medium

LI Jin-feng et al. [14] also experimented with the corrosion of 2195 Al-Li alloy by the method of studying 1420 Al-Li alloy. The results show that the 2195 Al-Li alloy under stress-free loading has general corrosion and local corrosion, including intergranular corrosion and pitting corrosion. When the stress is applied (the yield strength is close to 490 MPa), the intergranular corrosion of the 2195 Al-Li alloy is more serious, resulting in severe general corrosion from the joint pit, as shown Fig.4. The 2195 Al-Li alloy under stress loading has more serious general corrosion and local corrosion than the 1420Al-Li alloy, which means that the tensile stress has more corrosion effect on the 2195 Al-Li alloy than the 1420 Al-Li alloy.
Figure 4. Corrosion morphology of 2195 Al-Li alloy without stress (a) and stress (b) for 3d

J.F.Li et al. [18] studied the exfoliation corrosion and electrochemical impedance spectroscopy of a certain type of Al-Li alloy (Al-2.8%Cu-1.5%Li-0.3%Mg-0.3%Zn-0.3%Mn-0.15%Zr) in EXCO solution under different aging conditions. They found that the equilibrium precipitates at grain boundaries increased with aging time. These equilibrium precipitates were anodic to the alloy matrix, so they became more sensitive to corrosion on the adjacent periphery. Therefore, the sensitivity of Al-Li alloy to exfoliation corrosion increases with aging time. In the initial stage of immersion in EXCO solution, the EIS diagram of Al-Li alloy studied is shown as shown in the Fig.5. The EIS curve of Al-Li alloy is composed of the sag capacitive arc in the middle and high frequency band and the inductance in the middle and low frequency band. As the immersion time prolongs, serious pitting corrosion and exfoliation corrosion occur, and two capacitive arcs appear in the range of medium and high frequencies and medium and low frequencies. At the same time, the two capacitive arcs of underaged alloys appear later than peak aging and over aging, which indicates that underaged Al-Li alloys corrode slowly in EXCO solution.

Figure 5. Nyquist plots of (a) under-aged, (b) peak-aged and (c) over-aged Al-Li alloys at initial stage of immersion in EXCO solution

3.4. Corrosion of Al-Li-Cu alloy in acidic medium

Nikolaos D. Alexopoulos et al. [19] studied the corrosion resistance of the new Al-Li alloy (AA2198), and compared it with the commonly used Al alloy (AA2024). The samples before the test were pre-etched in the stripping corrosion solution (EXCO solution) for different time, and then the tensile properties of the two kinds of aluminum alloys were tested. The longer the time in the etching solution, the surface pits caused by corrosion have a far-reaching impact on ductility. They found that they found that after exposure for 2 hours, the tensile flow curve of AA2024 aluminum alloy suddenly decreased, and the strength of the material decreased due to a series of transverse cracks on the surface caused by corrosion, which resulted in the reduction of the finite thickness of the specimen. However, in the absence of deterioration of the surface, very short corrosion time cannot explain the decrease in tensile ductility, which is caused by the hydrogen embrittlement effect. Similarly, with the prolongation of corrosion time of AA2198 in EXCO solution, the elongation at break seems to decrease continuously. However, no sudden decrease in the strength of flow curve has been observed. The surface of typical AA2198 specimens at different corrosion times is shown in the Fig.6. As can be seen from Fig. 6a, the corrosion area of tensile specimens with low corrosion time is very limited, and the fracture path (6d) is
almost perpendicular to the direction of the applied axial load. Therefore, corrosion time has little effect on fracture mechanism. In Fig.6b, more pitting corrosion appeared on the surface of the corroded specimens. Fig.6e showed that the fracture path of the specimens followed the weakest ligament in the specimens. The surface cracking density caused by tensile was also obvious. Finally, the excessive surface degradation caused by corrosion was shown in Fig.6c. After 48 hours of corrosion, small scale pitting and excessive exfoliation can be seen. Generally speaking, it can be confirmed that Al-Li alloy (AA2198) has an advantage in corrosion resistance compared with ordinary aluminum alloy, and its initial tensile properties can maintain a higher percentage (89%) while AA2024 can only maintain about 70%.

![Figure 6](image)

**Figure 6.** Typical corroded surfaced of tensile specimens of AA2198 for different exposure time: (a)2h, (b)24h, (c)48h; and (d) to (e) respective surfaces after tensile tests

LUO Chen et al. [20] first carried out anodic oxidation of 2A97 Al-Li alloy cold-rolled sheet samples in boric acid-sulphuric acid solution and salicylic acid-sulphuric acid solution, and then exposed them to Wanning Natural Environment Test Station in Hainan for experimental analysis. They found that at higher temperatures, the higher the current density passed, the faster the growth of the electrolyte. After SEM observation, there are continuous porous membranes on the surface of two different electrolytes after anodizing, and the structure and technological properties of the pore are similar. The samples after anodizing with boric acid-sulphuric acid solution appear dispersive black rust spots after one-month exposure in tropical marine atmospheric environment, which are mainly composed of O, Al, Cl and a small amount of Cu elements by EDS analysis. At the same time, white precipitation occurs on the surface of the sample; with the increase of exposure time, serious pitting corrosion occurs and gradually penetrates into the alloy

### 4. Conclusion

Exposure of aluminum and its alloys in various acidic environments leads to corrosion, resulting in material damage and consequent economic losses. From the above analysis, it is found that the corrosion of aluminum-lithium alloy in acidic environment is mainly pitting corrosion. With the increase of corrosion time, the increase of temperature and other factors, the area and depth of corrosion pits become larger and larger, and then exfoliation corrosion occurs. In order to ensure the effective use of Al-Li alloys, we still have a lot of work to do:

1. Need to carry out specific research on various types of aluminum-lithium alloys;
2. Simulate corrosion medium in various cases for research;
3. Conduct different heat treatment and welding methods to study the effect of different microstructures on the corrosion properties of the alloys;
4. The structural analysis, corrosion performance and mechanical properties of the alloy were systematically analyzed and evaluated.

As people pay more and more attention to aluminum-lithium alloys, research is gradually deepened and new technologies and new processes appear, and the development trend of future aluminum-lithium alloys is predicted as follows:

1. Focusing on weight reduction first, followed by performance, and finally returning to the road of taking into account mechanical properties, weight loss, process performance and cost. Future aluminum-lithium alloys should have low anisotropy, high performance and low cost.
2. Inseparable from the progress of the process technology, gradually developed from riveting to welding, from forging thin-walled parts to integral machining of thick-walled parts, and then to laser/stirred friction welding to deepen the overall processing technology.
2. With the advancement of material preparation technology, the scope of application has been continuously expanded, from skin to wall to welded overall structure.

References
[1] Yin Dengfeng, Zheng Ziqiao. History and present situation of research and development of Al-Li Alloys[J]. Materials Review, 2003, 179(2): 18-20.
[2] Rioja R J. Isotropic Wrought Aluminum-Lithium Plate Development Technology[J]. Materials Science and Engineering A, 1998, 257(1): 100-107.
[3] Yuan Z S, Lu Z, Xie Y H, et al. Mechanical properties of a novel high-strength aluminum-lithium alloy[J]. Mater Sci Forum, 2011, 689: 385.
[4] Friedlander I N, Bratukhin A G, Davydov V A, Soviet Al-Li Alloys of Aerospace Applications[C]. Garmisch Partenkirchen: DMG Verlag, 1992: 35-42.
[5] Campbell FC. Manufacturing technology for aerospace structural materials[J]. Elsevier; 2006.
[6] Williams JC, Starke EA. Progress in structural materials for aerospace systems[J]. Acta Mater 2003; 51: 5775-99.
[7] Giummarrar, Thomas B, Rioja RJ. New aluminum lithium alloys for aerospace applications[C]. In: Light metals technology conference; 2007.
[8] Kalyanam S, Beaudoin AJ, Dodds Jr RH, Barlat F. Delamination cracking in advanced aluminum–lithium alloys-experimental and computational studies[J]. Eng Fract Mech 2009; 76: 2174-91.
[9] Soboyejo WO, Srivatsan TS. Properties, design optimization and applications[M]. Taylor & Francis Group, LLC; 2006.
[10] GRUENBERG K M, CRAIG B A, HILLBERRY B M, et al. Predicting Fatigue of Pre-corroded 2024-T3 Aluminum[J]. International Journal of Fatigue, 2004, 26(6): 629-640.
[11] BELLINGER N C, KOMOROWSKI J P, BENAK T J. Residual Life Predictions of Corroded Fuselage Lap Joints[J]. International Journal of Fatigue, 2004, 21(1): 349-356.
[12] SABELKIN V, PEREL V Y, MISAK H E, et al. Investigation into Crack Initiation from Corrosion Pit in 7075-T6 under Ambient Laboratory and Saltwater Environments[J]. Engineering Fracture Mechanics, 2015, 134: 111-123.
[13] MEDVED J J, BRETON A M, IRVING P E. Corrosion Pit Size Distributions and Fatigue Lives: a Study of EIFS Technique for Fatigue Design in the Presence of Corrosion[J]. International Journal of Fatigue, 2004, 26: 71-80.
[14] LI Jin-feng, CHEN Wen-jing, ZHAO Xu-shan, et al. Corrosion behavior of 2195 and 1420 Al-Li alloys in neutral 3.5% NaCl solution under tensile stress[J]. Transactions of Nonferrous Metals Society of China, 2006, 16: 1171-1177.
[15] C.-X. Li, X. Tan, J.F. Li*, et al. Corrosion behavior of 1420 Al-Li alloy under MgCl2 drops in 33% relative humidity[J]. Materials and Corrosion, 2014(65): 476-483.
[16] Conde A, de Damborena J. Corrosion behaviour of nitrogen implanted titanium in simulated body fluid[J]. Corros Sci, 2000; 42: 1393.
[17] SU Yan, ZHANG Lun W, ZHONG Yong. Marine Atmospheric Corrosion Behavior of 5A90 Al-Li Alloy[J]. Journal of Chinese Society for Corrosion and Protection, 2016, 36(3): 260-266.
[18] J.F.Li*, Z.Q.Zheng, S.C.Li, et al. Exfoliation corrosion and electrochemical impedance spectroscopy of an Al-Li alloy in EXCO solution[J]. Materials and Corrosion, 2007, 58: 273-278.
[19] Nikolaos D. Alexopoulos*, Angleiki Proiou, Wolfgang Dietzel, et al. Mechanical properties degradation of 2198 alloy due to corrosion exposure[J]. Procedia Structural Integrity, 2016(2): 597-603.
[20] LUO Chen, Sergiu P, Albu, et al. Mechanism of Early Stage Corrosion for Boric-sulfuric Acid Anodized 2A97 Al-Cu-Li Alloy Under Tropical Marine Atmosphere[J]. Journal of Materials Engineering, 2016, 44(9): 8-15