Evolution Laws of 7B04 Aluminum Alloys Pitting Corrosion Topography Characteristics and Size Parameters

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Abstract: Pitting corrosion is a typical damage of aircraft aluminum alloys structure which is attacked by the chloride ions in service environment, and the corrosion pit topography characteristics will eventually affects the fatigue property of aluminum alloys structure. In order to obtain the evolution laws of corrosion pit topography in different corrosion period, the pitting corrosion test of 7B04 aluminum alloy specimen was carried out according to the accelerate corrosion test environment spectrum which was programmed from the true service airport environment data, based on the electrochemical corrosion mechanism of aluminum alloy pitting corrosion and the accelerated corrosion test result, the evolution laws of 7B04 aluminum alloy pitting corrosion topography characteristics during different corrosion period was analysed through the corrosion topography parameter C which was defined by the pit surface area and the least rectangle area of the typical corrosion pit area, it was found that the C parameter gradually tended to be 0.8 with the corrosion period prolongation which indicated that the corrosion pit surface geometry inclined to be circle or ellipse. The evolution laws of 7B04 aluminum alloys pitting corrosion topography characteristics could set research base for further corrosion fatigue life analysis of the aircraft 7B04 structure.

Introduction

The fatigue crack of aircraft aluminum alloy structure is usually initiated from the pit corrosion damage, and the whole corrosion fatigue process often includes the following stage, firstly pitting corrosion initiation, then corrosion pit growth and the transition from pit to crack and lastly crack growth and fracture and so on[1-3],so the behavior of pitting corrosion initiation and growth is of vital importance to the corrosion fatigue analysis of aircraft aluminum alloy structure, in other words the research of corrosion pit and its relevant knowledge are the basic part of corrosion fatigue life analysis field, especially the corrosion pit topography characteristics would directly affect the nucleation site and the initial size and the geometry characteristics of fatigue crack which are the key parameters to the corrosion fatigue life analysis[4-7],so it is of great worth to carry out the mentioned context research.

Pitting corrosion of aircraft aluminum alloy structure is a result of failure of the passive film which is usually broken down in the presence of chlorides in the service environment[8],the typical aircraft 7B04 aluminum alloy is chosen as research object, and the accelerated pit corrosion test which includes soaking in the corrosion solution and raying out of solution was carried out to reappear the pitting corrosion progress and pitting corrosion pattern of aircraft aluminum alloy structure pitting corrosion in the true service environment, then the the corrosion pit damage data was obtained through microscope and anaysed by the statistical anaysis method, in the end pitting corrosion topography characteristics evolution law of 7B04 aluminum alloy was obtained by modelling according to the corrosion test data and the electrochemical corrosion mechanism which set basis for the corrosion fatigue life analysis of aircraft aluminum alloy structure.
Pitting Corrosion Test

The dimension of 7B04 aluminum alloy specimen is shown as figure 1 which was cleaned with the absolute ethyl alcohol in order to get rid of the impurity of the specimen surface, the composition of 7B04 aluminum alloy is shown in table 1.

![Figure 1. The dimension of specimen.](image)

| Element | Cu   | Mg   | Mn   | Zn   | Si   | Fe  | Ti   | Be   | Al   |
|---------|------|------|------|------|------|-----|------|------|------|
| Content(%) | 3.8~4.3 | 1.7~2.3 | 0.4~0.9 | <0.1 | <0.2 | <0.3 | <0.1 | 0.0002~0.005 | the others |

It is a long period method that putting the specimen in the true aircraft service environment to initiat natural pitting corrosion and obtaining the dimensions parameters of corrosion pits, so in order to reduce the research time and simulate the aluminum alloy pitting corrosion process in the service environment, the accelerated pitting corrosion test was carried out according to the environment spectrum which was calculated from the true data of service environment factors with statistical method and was depicted as shown in figure 2[9-10], and the test equipment was ZJF-75G periodic soaking test cabinet. During the corrosion test process, the 80 individual specimen was laid in the bracket with equal distance to guarantee the test result valid from statistics perspective.

![Figure 2. Accelerated corrosion test environment spectrum.](image)

The accelerated corrosion test lasted 400 hours in accordance with HB455-90 standard, every specimen was picked out with fixed test period to be observed and the dimension of corrosion pits was gauged through KH-7700 three dimensional microscopy, and the typical macroscopic corrosion topography of samples in different corrosion period was shown as in figure 3 in which the corrosion pits sites and pit corrosion density increased with the corrosion period prolongation.

![Figure 3. Macroscopic corrosion topography of typical 7B04 samples.](image)
The Electrochemical Corrosion Mechanism of Pitting Corrosion

The basis of the pitting corrosion topography analysis is galvanic coupling corrosion mechanism. From the table 1, it can be concluded that the 7B04 aluminum alloy includes some others elements besides the Al element, according to the literature, there are about average 2000 constituent particles on the 1 mm² surface of material, among them, such as the Cu, Fe particle[11-13], act as cathodes, and the surrounding aluminum acts as an anode when the alloy is immersed in the electrolyte, so the base metal Al adjacent to the cathodic particle dissolves electrochemically and this process leads to the initiation of a corrosion pit, the reaction between the cathodes and the anode could be depicted as followed:

\[ \text{Al} + 3\text{e}^- \rightarrow \text{Al}^{3+} \]  
\[ \frac{3}{2}\text{O}_2 + 3\text{H}_2\text{O} + 6\text{e}^- \rightarrow 6\text{OH}^- \]  

From the equation, it can be regarded that the aluminum alloy gradually dissolved with the pitting corrosion initiation and the geometric dimension parameters of corrosion pit increased with the corrosion in progress. The initiation progress of 7B04 specimen surface pitting corrosion was observed through the SEM and was depicted in figure 4.

![Figure 4. SEM micrographs of 7B04 specimen corrosion pit initiation.](image)

The Evolution of Pitting Corrosion Topography

From the figure 4, it could be seen that the pitting corrosion initiates from the particles which are distributed on the specimen surface randomly, the pitting corrosion is a stochastic process in essence[14-15] which leads the corrosion pit topography to randomness in geometry appearance. In this paper, the corrosion pit topograph parameter \( C \) was defined as showed in equation (3) and in figure 5 which was used to depict the surface geometry of typical corrosion pits, it can be seen that the parameter \( C \) represents the ratio of the corrosion pit surface area and the least rectangle area which surrounds the corrosion pit.

\[ C = \frac{S_p}{S_R} \]  

![Figure 5. Typical microscopic appearance of 7B04 specimen surface pitting corrosion.](image)
In equation (3), the $S_p$ represents the true corrosion pit surface area which can be measured through microscope and its software, and the $S_r$ represents the least rectangle area which surrounds the corrosion pit, the unit of $S_p$ and $S_r$ are $\mu m^2$. According to the definition of the parameter $C$, we can conclude that the pit surface geometry links with the value of the $C$, for example, if the pit surface geometry is triangle, $C \approx 0.5$; if the pit surface geometry is rectangle, $C \to 1$; likely, if the geometry of pit surface is circle or ellipse, $C \approx \pi/4 \approx 0.8$.

Between certain corrosion interval, 3 specimen were brought out from the corrosion solution and 20 typical corrosion pits on every sample were chosen which were measured through three dimensional microscope to obtain the data of pit area and least rectangle area that surrounding the pit, so there were 60 data at every corrosion interval which were used to analyse the pit topography and its evolution law. The analysis results were depicted in figure 6 during different corrosion period.

As illustrated in figure 6, the $C$ parameter gradually tended to be 0.8 with the corrosion time prolongation in the former corrosion period which indicated that the surface geometry of corrosion pits inclined to be circle or ellipse, contrastly the parameter $C$ exhibited irregular pattern in the later corrosion progress which was owed to the coalescence of different corrosion pits with the corrosion period prolongation and pit density increasement, the coalescence of pits was as shown in figure 7 which obtained through SEM micrograph. Based on corrosion test results, the pitting corrosion of aluminum alloy could transform to exfoliation which was not to be discussed in this paper.

Figure 6. The evolution laws of specimen pitting corrosion topography characteristics.

Figure 7. SEM micrographs of specimen surface during later pitting corrosion stage.
The Evolution of Pitting Corrosion Size Parameters

During the progress of aluminum alloy pitting corrosion, the corrosion pit also gradually extends to the interior of material matrix besides the surface topography changing. The prevailing view is that the expanding of aluminum alloy pitting corrosion follows the Faraday's law[16-19], combing the Arrhenius equation, the expanding model of aluminum alloy pitting corrosion can be depicted as followed expression,

\[
\frac{dV}{dt} = \frac{MI_p}{nF\rho} = \frac{MI_{p_0}}{nF\rho} \exp\left(-\frac{E_a}{RT}\right)
\]

(4)

\[
I_r = I_{p_0} \exp\left(-\frac{E_a}{RT}\right)
\]

(5)

In equation (4) and (5), the \(V\) represents the volume of corrosion pit, and \(t\) represents the corrosion time, \(M\) is atomic weight, \(I_p\) is the corrosion current density, and \(I_{p_0}\) is corrosion current density constant, \(n\) is valency, \(F\) is the Faraday constant, \(\rho\) is material density, \(E_a\) represents the activation energy, \(R\) is ideal gas constant, and \(T\) is the absolute temperature.

Based on the analysis results of corrosion pit topography evolution, the corrosion pits were viewed as hemispheroid, so the evolution rules of corrosion pits size parameters could be depicted as followed expression,

\[
V = \frac{2}{3} \pi a^3
\]

(6)

In the equation, \(a\) represents the radius of corrosion pit, adopt differential operation to equation (6),

\[
\frac{da}{dt} = \frac{dV}{dt} \cdot \frac{1}{2\pi a^2} = \frac{1}{2\pi a^2} \frac{dV}{dt} = \frac{1}{2\pi a^2} \frac{MI_p}{nF\rho}
\]

(7)

The evolution rule of corrosion pits radius with corrosion periods can be obtained through integration equation (7).

\[
a = \left[ \frac{3MI_p}{2\pi nF} \cdot t + a_0^3 \right]^{\frac{1}{3}}
\]

(8)

\(a_0\) represents the initial corrosion pit radius, and its unit is \(\mu m\).

The value of mentioned parameters was defined according to the literature[17-18], the corrosion pits size value in different corrosion time could be calculated which showed in table 2, the test results also showed in table 2 which illustrated that the equation (8) reasonably reflected the evolution of pitting corrosion size parameters.

| Table 2. Comparison between test results and model calculation of corrosion pit size a. |
|-----------------------------------------------|---------|---------|---------|
| Corrosion time/h                            | 100h    | 200h    | 400h    |
| Accelerated corrosion test/\(\mu m\)         | 18      | 25      | 42      |
| Equation (8)/\(\mu m\)                       | 21      | 29      | 48      |
| Relative error(%)                            | 16.7    | 16      | 14.3    |

Conclusion

Based on the accelerated corrosion test result of 7B04 specimen and the statistical analysis method and the electrochemistry mechanism, the corrosion pit topography characteristics is discussed.
The pit surface geometry inclines to be circle or ellipse in the former corrosion period and exhibits irregular pattern because of the coalescence of different corrosion pit in the later corrosion period.

If the corrosion pit is viewed as hemispheroid, the corrosion pit size parameter $a$ is modelled with corrosion time $t$ and the relative error between test and model calculation is better agreement.

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