# Influence of Contaminated $NH_3$ on Stress Corrosion Behavior of 7075 High Strength Aluminum Alloy in Marine Atmosphere Environment

**Peiling Yan**
College of Chemistry and Chemical Engineering, Qingdao University, Ningxia Road, Qingdao, China
904420552@qq.com

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**Abstract:** The addition of $NH_4^+$ in NaCl which could simulate the marine atmosphere environment contaminated $NH_3$accelerates the corrosion process of 7075 high strength aluminum alloys. The acceleration effect is mainly promoted by the reaction process of aluminum alloy cathode. This is due to the fact that $NH_4^+$ leads to the acidification of solution to promote the occurrence of cathodic reaction. The addition of $NH_4^+$ increases the stress corrosion susceptibility of the 7075, and the sensitivity of stress corrosion increases with the increase of $NH_4^+$ concentration. The reason is that the acceleration of the cathodic reaction process caused by $NH_4^+$ promotes the precipitation of hydrogen and the diffusion in the aluminum alloy. At the same time, the corrosion effect of the aluminum alloy also changes the mechanical properties of the aluminum alloy, and the stress corrosion sensitivity of the high strength aluminum alloy increase.

## 1. Introduction

7075 high-strength aluminum alloy has been widely used in the aviation industry due to the high strength and low density. However, in the marine atmospheric environment, high-strength aluminum alloy prone to pitting, intergranular corrosion and peel corrosion, or even stress corrosion cracking. It is a serious threat to the safety of equipment services made of 7075.

At present on the corrosion of aluminum alloy in the natural environment has been carried out a certain study [1-7]. Researchers found traces of pitting [1-5], intergranular corrosion [3, 6, 7], peel corrosion [6, 7] and stress corrosion cracking [3]. Sun et al. [6] studied the corrosion behavior of 7075 aluminum alloys in rural, marine and industrial environments atmosphere, and found that the aluminum alloy was significantly eroded with peel corrosion and resulted in a significant decrease in mechanical properties. Based on the literature resources, we found that the study of stress corrosion of high strength aluminum alloys in the atmosphere is still small. We believe that this is because the natural environment corrosion test generally needs a long time, but the completed test is mainly concerned with the weight loss and morphology change for the corrosion. It is difficult to carry out in-depth study of its stress corrosion behavior.

Recently, researchers usually use the tensile test in the solution for the study of stress corrosion of aluminum alloy [8-10]. But in the marine atmosphere, the essence of aluminum alloy corrosion is the electricity chemical process in unsteady thin electrolytes layer whose thickness, shape and distribution will be of cyclical changes due to temperature, humidity, light, rainfall and other factors with alternating effects. The unsteady characteristics of the thin film are mainly manifested in the dynamic and dispersive, dynamic can lead to thin film thickness from several molecular layer to several millimeters change, and the dispersion leads to material, liquid film and gas composition Of the "gas / liquid / solid" three-phase interface area increased[11]. Stratmann et al. [12] found that with the decrease of liquid film, the rate of oxygen reduction under thin film increases first and then decreases. The dispersibility of the liquid film will lead to further changes in the electrode reaction process. Wang et al. [11] found that the cathodic limit diffusion current density and the corrosion current density increase linearly with increasing three-phase length. The change of electrochemical process will further affect the change of stress corrosion behavior of aluminum alloy. Therefore, to study of stress corrosion behavior of high strength aluminum alloy under unsteady thin film is beneficial to the deep understanding of the corrosion of aluminum alloy in marine atmosphere.

In addition, environmental factors have an important effect on the composition and morphology of liquid films and stress corrosion processes. The change of environmental factors, such as temperature, humidity, $Cl^-$concentration and pollutants, has great influence on the stress corrosion of the material with the change of the latitude and longitude of the earth and the coastal geography. $NH_3$ is the main component of the contaminated marine atmosphere which contaminating $NH_3$ can lead to the acidification of the thin liquid film. This must affect the electrode reaction process, especially the hydrogen permeation behavior, which affects the development process of stress corrosion [13]. For this reason, it is very important to study the stress corrosion of high strength aluminum alloy under the environment of marine atmosphere with the pollutant $NH_3$.

In this paper, 7075 aluminum alloy was selected as the samples of study. To simulate the polluted marine atmosphere, we mix different concentrations of $NH_4Cl$ in 3.5% NaCl solution. By slow strain rate tensile test, the stress corrosion behavior and stress corrosion mechanism of 7075 aluminum alloys was studied.

## 2. Experimental sections

### 2.1. Sample preparation

Figure 1 is the tensile specimen in the SSRT tests.

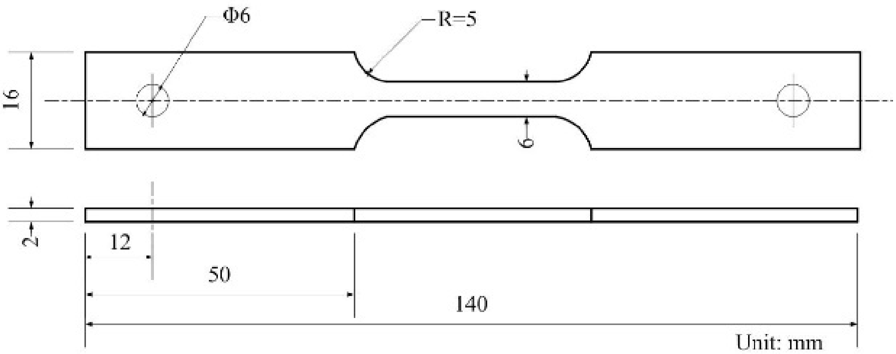


Fig 1 Geometry of the tensile specimen for aluminum alloy used in the SSRT tests

The purchased 7075 aluminum alloy sheets were subjected to electrical discharge machining and the specimen in Figure 1 were obtained. Before each test, the four surfaces of the test area were polished with 1500# abrasive paper, and the scratch orientation was consistent.

### 2.2. Experiment method

Slow strain rate tensile (SSRT) test is the main method in this paper.

Strain rate parameter is an important parameter of the slow strain rate tensile test, 0.0018 mm/s in this experiment. The tensile test software was opened in the computer connected with the testing machine is connected with the computer set the parameter, and start the test. The experiment simulation corrosion medium selected in this experiment is as shown in Table 1.

Table 1 Design of experimental variables for SSRT

| State of corrosive medium | Corrosive medium variable |
|---|---|
| 25°C Atmospheric gas state | Air medium |
| | 3.5% NaCl |
| | 3.5% NaCl + 0.001mol/L $NH_4Cl$ |
| | 3.5% NaCl + 0.01mol/L $NH_4Cl$ |
| | 3.5% NaCl + 0.1mol/L $NH_4Cl$ |

The humidity of the gaseous corrosion medium environment simulated in this experiment is above 98%. The gauge length of all polished samples, average width and average thickness of the test area should be measured before the test. In the simulated gaseous corrosion medium, the test needs pre-corrosion for 12 hours in the absence of stress, and then the stress tensile test is implemented. The simulated gaseous corrosion medium should be sealed by silica gel, as shown in Figure 2. Only the test area of 20mm in the specimen sample is retained to prevent from affecting the accuracy of the test result because of the development and progression stress corrosion in the non test area exposed to the corrosive medium.In the simulated gaseous corrosion medium, an organic glass box is used as the container holding medium in the test. At the test, the sample specimen was conducted with rust removal to prepare the SEM for observing the fracture surface.

## 3. Result and discussion

### 3.1. Slow strain rate tensile curve

7075 specimen sample is conducted with SSRT tests in different corrosive mediums, and the stress-strain image is as shown in Figure 2. The experiment result is discussed according to 7075 stress-strain curve and data parameter.

### 3.2. Tensile strength

Tensile strength $\sigma_{max}$ refers to the maximum uniform plastic deformation force that a material can withstand. In Figure 2, the tensile strength is the force corresponding to Point B. By comparing the 7075 stress-strain curve, it can be found that the tensile strength of the sample is the largest in the air medium. After corrosive gas is introduced, the tensile strength decreases. After 3.5% NaCl spray corrosive gas is introduced, with the increase of $NH_4Cl$ concentration in the medium, the tensile strength decreases.

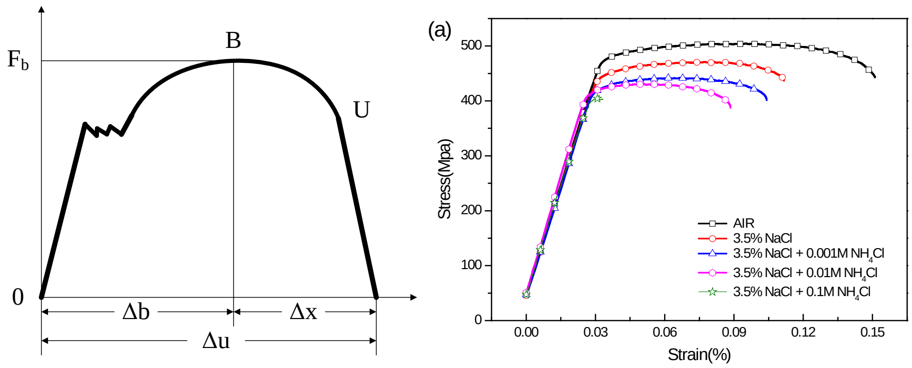


Fig 2 Stress strain curves of the 7075 samples in diffident corrosion medium

### 3.3. Strain

Strain $\varepsilon$ refers to the amount of deformation in which the material is subjected to force, namely, Δu. In this experiment, the strain is the amount of stress at which the sample is stretched. According to 7075 stress-strain curve, it can be found that the sample has the largest strain in the air medium. After the corrosive medium is introduced, the strain of the sample decreases. With the increase of $NH_4Cl$concentration in corrosion medium, the strain of the sample continuously decreases.

### 3.4. Integral area of stress-strain curve

Table 2 Parameters of stress-strain curve for 7075

| Corrosive medium environment | $\sigma_{max}$ (MPa) | elongation at break (%) | Integral area of stress-strain curve *S* |
|---|---|---|---|
| Air | 503.86 | 14.9 | 66.99 |
| 3.5% NaCl | 472.11 | 10.96 | 44.83 |
| 3.5% NaCl + 0.001mol/L $NH_4Cl$ | 445.38 | 11.05 | 40.25 |
| 3.5% NaCl + 0.01mol/L $NH_4Cl$ | 435.26 | 9.03 | 31.98 |
| 3.5% NaCl + 0.1mol/L $NH_4Cl$ | 400.18 | 4.05 | 9.05 |

The integral area of stress-strain curve can characterize the toughness of the test material. Greater integral area indicates that the material has better toughness. Therefore, the integral area of stress-strain curve in corrosion is generally greater than that without corrosion. In this experiment, the necking of the samples caused by tensile stress in corrosive medium is significantly smaller than that in the air medium. This shows that the roughness of the sample decreases. This phenomenon can be verified by integral area of the stress-strain curve. The above three parameters are summarized in Table 2.

According to HB72395, the stress corrosion fracture sensibility can be determined by two methods: One is the ratio of percentage reduction of area. That is, the stress corrosion sensibility can be determined by the ratio of the percentage reduction of area of the material in the corrosive medium to that in the air medium. The formula is $\Psi_{condition}/\Psi_{inertenvironment}(\Psi_c/\Psi_i)$. When the ratio is smaller than 95%, it is believed that the material has a sensitivity to stress corrosion. Moreover, the smaller the ratio is, the greater the stress corrosion sensibility will be. The other is $I_{SSRT}$ index, and the basic formula is as follows:

$$I_{SSRT}=1-\frac{\sigma_{fW}\cdot(1+\delta_{fW})}{\sigma_{fA}\cdot(1+\delta_{fA})} \tag{1}$$

Where, $\sigma_{fW}$ is the fracture strength of the sample in the corrosive medium;

$\sigma_{fA}$ is the fracture strength of the sample in the air medium;

$\delta_{fW}$ is the elongation at break of the sample in the corrosion medium;

$\delta_{fA}$ is the elongation at break of the sample in the air medium.

The value of $I_{SSRT}$ changes between 0 and 1. The bigger the value, the stress corrosion sensitivity is higher.

In the actual test, the fracture shape of the two kinds of aluminum alloy is complicated after stress corrosion, and the manually measured fracture size has large errors. Therefore, in order to improve the accuracy of fracture area data, the formula as below is used to calculate the value.

$$S=\left(\frac{S_0L_e}{L_e+\Delta b}\right)\left(\frac{\Delta b}{F_b}\right)\left(\frac{F_u}{\Delta u}\right) \tag{2}$$

Where, $S_0$ is the original cross sectional area of the sample;

$Le$ is the original gauge length of the sample;

$F_u$ is the stress at which the sample breaks;

$F_b$ is the stress corresponding to tensile strength (Point B);

$\Delta b$ is the strain corresponding to Point B (elongation);

$\Delta u$ is the strain corresponding to the fracture of the sample (elongation).

According to the above formula, the experimental data are summarized and the parameters required to calculate the fracture area are obtained, as shown in Table 3.

Table 3 Calculation parameters of fracture area for 7075

| Corrosive medium | Fracture strain(N) | Elongation at rupture(mm) | Strain at Point B(N) | Elongation at Point B(mm) | Fracture area ($mm^2$) |
|---|---|---|---|---|---|
| Air medium | 4408.50 | 4.36 | 5135.40 | 2.81 | 4.74 |
| 3.5% NaCl | 4713.89 | 3.59 | 5085.54 | 1.90 | 5.18 |
| 3.5% NaCl + 0.001mol/L $NH_4Cl$ | 4215.53 | 3.45 | 4689.55 | 1.685 | 5.42 |
| 3.5% NaCl + 0.01mol/L $NH_4Cl$ | 3911.54 | 2.77 | 4311.52 | 1.73 | 5.87 |
| 3.5% NaCl + 0.1mol/L $NH_4Cl$ | 4198.20 | 1.13 | 4199.46 | 1.10 | 11.44 |

According to the data in Table 4, in terms of $\Psi_c/\Psi_i$ criteria, the stress corrosion sensitivity of 7075 aluminum alloy increases with the concentration of $NH_4$Clin corrosive medium. As for $I_{SSRT}$ index criteria, 7075 shows the same stress corrosion sensitivity change trend as above. It should be noticed the data in the table shows that 7075 sample in 3.5% NaCl, $\Psi_c/\Psi_i$=98.31%>95%, which is smaller than 100%. However, in the same condition, $\Psi_c/\Psi_i$=98.31%>95%. Therefore, it is believed that 7075 has stress corrosion sensitivity in this state.

Table 4 Parameters and criteria of the stress corrosion sensitivity of 7075 samples

| Corrosive medium environment | Original cross sectional area($cm^2$) | Fracture area ($cm^2$) | Percentage reduction of area (%) | $\Psi_{environment}/\Psi_{air}$ (%) | $I_{SSRT}$ | SCC Sensitivity |
|---|---|---|---|---|---|---|
| 3.5% NaCl | 10.82 | 5.15 | 51.99 | 98.31 | 0.25 | Sensitive |
| 3.5% NaCl + 0.001mol/L $NH_4Cl$ | 10.82 | 5.19 | 52.03 | 94.22 | 0.33 | Sensitive |
| 3.5% NaCl + 0.01mol/L $NH_4Cl$ | 9.86 | 5.45 | 44.36 | 82.99 | 0.52 | Sensitive |
| 3.5% NaCl + 0.1mol/L $NH_4Cl$ | 10.530 | 10.20 | 3.25 | 5.89 | 0.84 | Sensitive |

## 4. Analysis of experimental results

The stress corrosion mechanism is divided into anodic dissolution type; hydrogen induced cracking type and mixed type of the two. Burleigh [14] reviewed the earlier research on aluminum alloy SCC and believed that anodic dissolution type SCC mainly occurs in Al-Cu-Mg alloy, while hydrogen induced cracking type SCC exists in Al-Zn-Mg-Cu alloy. In contrast, a great number of later researches argued that the synergy mechanism of the two types can better explain the essence of high strength Aluminum Alloy SCC [8-10]. In this paper, the addition of significantly promoted the stress corrosion behavior of the two kinds of high strength aluminum alloy. This should be explained from the following perspectives. Firstly, the addition of $NH_4^+$accelerated the corrosion behavior of the two types of aluminum alloy, and the reduction of aluminum alloy caused by corrosion will reduce its mechanical properties. The hydrogen produced in corrosion further affects the SCC behavior of aluminum alloy. In the stress corrosion of aluminum alloy in medium, the cathodic hydrogen evolution reaction makes the atomic hydrogen enter into the sample and enrich at the crack tip, which has been verified by many experiments. Meantime, corrosion reduces the mechanical properties of the material. Therefore, under the combined action, SCC sensitivity of aluminum alloy increases rapidly. The fracture angle gradually changes from 45° to the direction perpendicular to the tensile stress, and the stress corrosion characteristics become more obvious.

## 5. Conclusions

In this paper, the influence of $NH_4^+$on the stress corrosion behavior of high 7075 aluminum alloy in $Cl^-$containing environment was investigated by analyzing the result of stress corrosion tensile test of samples in NaCl solution with $NH_4Cl$. The conclusions show that:

The $NH_4^+$ in the solution increases the stress corrosion susceptibility of the 7075, and the sensitivity of stress corrosion increases with increasing $NH_4^+$ concentration in the solution. The reason is that the acceleration of the cathodic reaction process caused by $NH_4^+$ promotes the precipitation of hydrogen and the diffusion in the aluminum alloy. At the same time, the effect of corrosion worsens the mechanical properties of the aluminum alloy and increases the stress corrosion sensitivity of the 7075 aluminum alloy.

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