

Uniform/Localized Corrosion and the Consequential Risks to Aircraft Aluminum Alloys

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High strength aluminum alloys are critical to aircrafts owing to their light weight, low cost, and outstanding corrosion resistance. Mechanical properties of aluminum alloys AA2024-T3 (UNS A92024), AA6061-T6 (UNS A96061), and AA7075-T6 (UNS A97075) were improved by forming precipitates (Al_2Cu , Mg_2Si , MgZn_2) and intermetallics (Al_2CuMg) in the matrix.¹ However, these second phases also introduced a higher corrosion susceptibility to aluminum alloys because of distinct interfaces which resulted in localized corrosion such as pitting corrosion and intergranular attack.²⁻⁷ Electrochemical difference at the interfaces of second phases increases corrosion susceptibility. Also, localized corrosion, which has a common form in pitting of aluminum alloys, tend to become initiation site of fatigue and cracking due to stress concentration especially under a cyclic loading. Pit growth kinetics in various water solutions was studied.⁸⁻¹⁰ Measuring pit growth rate in order to provide a precise prediction has become the primary interest of aluminum alloy corrosion.¹¹⁻¹⁴

As shown in Fig. 1, the pit depth growth rate becomes slower without considering uniform corrosion properly, where d_0 is the pit depth formed prior to uniform corrosion, d is the pit depth measured after uniform corrosion, and d' is the difference introduced by uniform corrosion. Therefore, the ability to measure pit depths and uniform corrosion by profilometric methods has become a critical correction to bridge the gap between practical and ideal pit growth kinetics. However, uniform corrosion was not thoroughly studied in the past in a quantitative

manner, and lacking the knowledge of uniform corrosion along with pitting has become a major challenge for pit growth prediction.

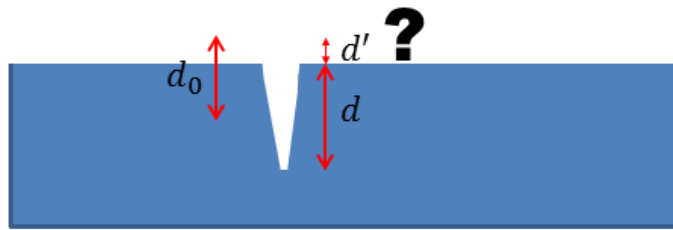


Figure 1 (a) Schematic of how uniform corrosion will affect the measured pit depth versus the values in the absence of any uniform corrosion

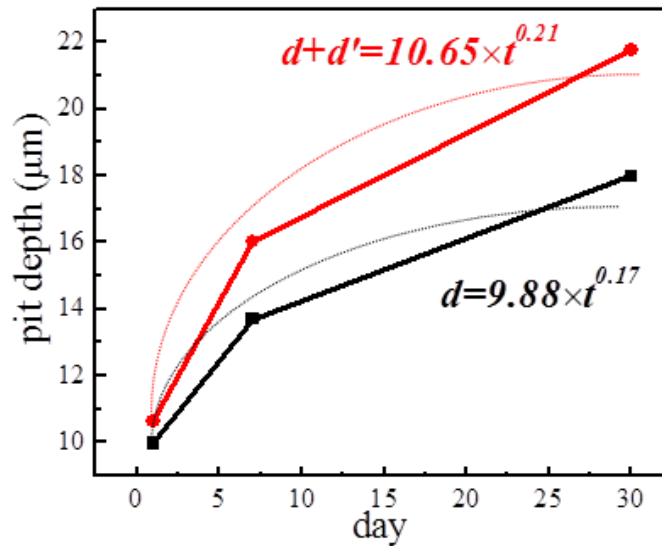


Figure 1 (b) Pit depth growth rate slowed by concurrent uniform corrosion

Weight loss experiment is one of the most efficient methods to assess uniform corrosion and has been performed to quantify corrosion rate of aluminum ¹⁵. The result suggests that pit volume fraction to the total weight loss is small, and a majority of aluminum weight loss is attributed to uniform corrosion ¹⁶. However, a quantitative measurement was not provided. In fact, lack of quantitative analysis of uniform corrosion versus pitting has caused confusion in analyzing the overall severity of corrosion. Therefore, pit growth kinetics has to account for the reference plane recession due to uniform corrosion. ^{4,17}

In order to obtain a quantitative assessment of uniform corrosion in fraction of the total weight loss, optical profilometry was utilized to acquire a quantitative measurement of pitting to uniform corrosion ratio. As shown in Fig 2, a comparison of volume loss attributed by pitting and overall material volume loss was observed that pitting is relatively minor in terms of overall material loss. According to this result, pitting of 2024 alloy contributed 20.7% of the total volume loss, 11.3% for 7075, and 3.5% for 6061 alloy. The ratio of pitting indicates the impact of pitting is highly proportional to the second phase fraction in each alloy that 2024 is more susceptible to pitting among these three while 6061 has the least attack by pitting. This result is due to the high Al_2CuMg (S phase) content in 2024 that prone to pitting, which was reported as the major cause of surrounding matrix dissolution.¹⁸ For 6061, the highest purity aluminum alloys among these three materials, has a minor Mg_2Si phase spread over the matrix without causing severe attack and relatively insoluble.¹⁹ 7075 alloy contain the most zinc which forms $MgZn_2$ as a strengthening factor, as well as more Mg and Cu. $MgZn_2$ is anodic to the matrix and less susceptible to pitting.²⁰ This makes 7075 as hard as many steels while still retaining the advantage of lightweight. This is a clear evidence to claim that uniform corrosion is significant to the entire weight loss, and will definitely alter observed pit geometry by lowering the reference surface.

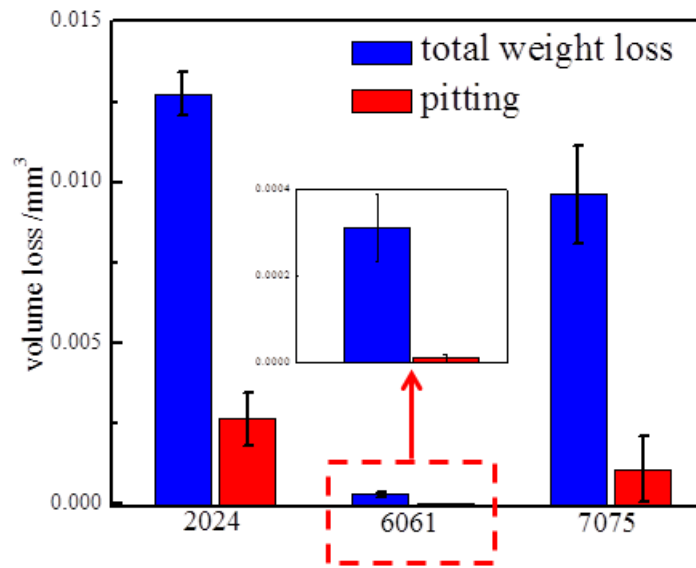


Figure 2 Weight loss experiment comparing versus summation of pit volume

In this work, pitting corrosion and uniform dissolution of aluminum alloys 2024-T3, 7075-T6 and 6061-T6 were characterized quantitatively using optical profilometry (OP) after free corrosion exposures in 0.01 to 1.0 M NaCl solutions as a function of pH, temperature and exposure time. Uniform dissolution was estimated by carefully measuring the step height between the masked surface and the exposed surface along with pitting information. All pitting information was collected on corroded surfaces. Three measurements were performed on each scan in order to obtain a complete measurement of entire surfaces. Pitting corrosion data (depth, area, and volume) were measured and analyzed for further comparison with aforementioned uniform corrosion.

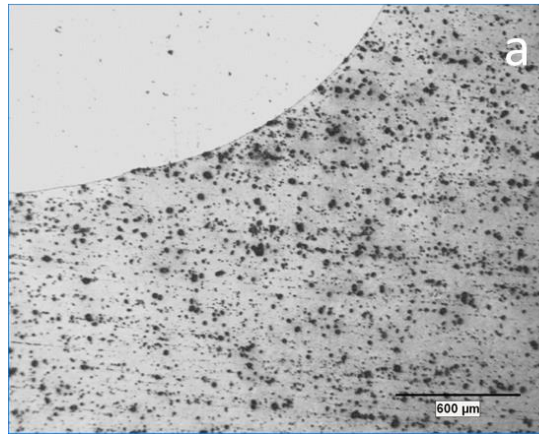


Figure 3 (a) Optical microscope image of protected and unprotected surface of 7075 alloy immersed in 1M NaCl solution at 40°C at pH10 for one month

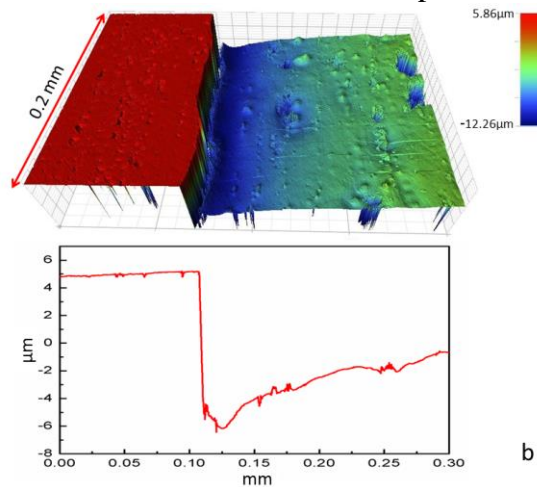


Figure 3 (b) OP image shows depth of 11.2 μm between protected/unprotected interface

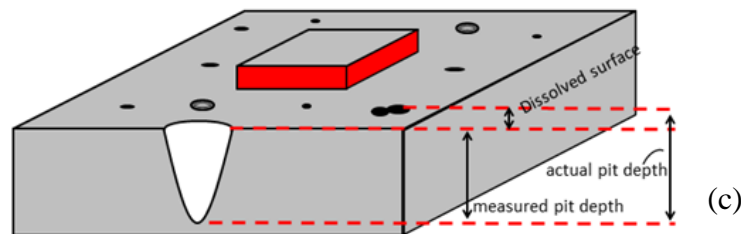


Figure 3 (c) schematic of sample analyzed after immersion test

Results showing that temperature and pH has a complex impact on Al alloy corrosion behavior. Under neutral and alkaline conditions, the corrosion rate of all three alloys at 80 centigrade had the lowest corrosion rate, appearing to be related to the fact that slowed oxygen reduction reaction. Oxygen reduction reaction (ORR) is the primary cathodic reaction to facilitate aluminum corrosion in atmospheric environment, while corrosion rate can be reduced

to one-third in deaerated solutions ²¹. In this regard, the corrosion reaction will be suppressed at high temperature since oxygen solubility is much lower ²². Therefore, to understand the interplay of temperature, ORR, and uniform corrosion rate is important for aluminum failure analysis.

Oxygen diffusion to the surface of aluminum can be the rate determine step in many cases, which can be described as limiting current density.

$$i_{lim} = \frac{nFDC}{\delta}$$

where n is charge carried by oxygen, F is Faraday constant, D is diffusivity, C is concentration, and δ is the characteristic diffusion length of oxygen on aluminum alloy surfaces. The diffusivity of oxygen can be characterized by

$$D = D_0 \exp\left(\frac{E_a}{RT}\right)$$

where D_0 is diffusivity at absolute zero, E_a is activation energy of diffusion. In this case D_0 for oxygen is 3.05×10^{-6} (m²/sec), and E_a is 1.79×10^4 (J/mol). ^{22,23} Also, the limiting current density is affected by the concentration of oxygen dissolved in water. The solubility of oxygen is decreasing with increasing temperature and the result with oxygen diffusivity is plotted in Fig. 4.

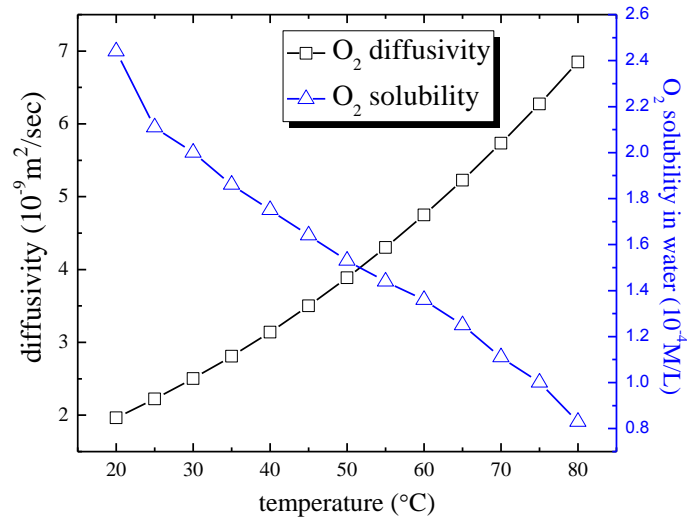


Figure 4 Oxygen solubility and diffusivity versus temperature in water

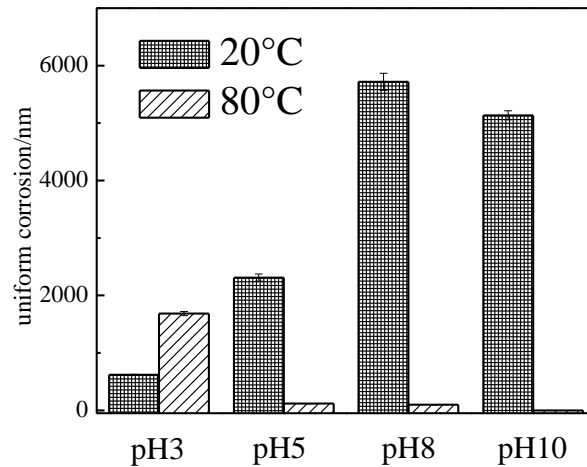


Figure 5 Uniform corrosion of 2024-T3 in 1M NaCl after one month immersion

Uniform corrosion result is shown in Fig. 5. A crossover trend with temperature change of uniform corrosion data is corresponding to the change of oxygen solubility. Uniform corrosion is suppressed at elevated temperature, while the supporting oxygen reduction reaction is decreased by its solubility. However, hydrogen evolution reaction is capable of supporting uniform corrosion at high temperature in acidic environment. Polarization test is a common

method to measure electrochemical reaction by manipulating the potential or current passing through a sample. This technique can provide further evidence of ORR decrease. In Fig. 6, the cathodic limiting current is reduced by oxygen solubility at elevated temperature. This is an evidence of suppressed oxygen reduction reaction (ORR) that lowered the uniform corrosion rate at high temperature. In addition, electrochemical impedance spectroscopy (EIS) result suggests that corrosion reaction is mass transport controlled at low temperature as shown in Fig. 7. At high temperature, the surface of aluminum alloys tends to form a film of hydroxide. A protective hydroxide layer preferably forming at high temperature hinders the path of oxygen can also reduce the cathodic current density. This film is inert to oxygen reduction reaction and protective to the matrix surfaces. In industry, boiling aluminum alloys in high temperature solutions is a common passivation treatment. Therefore, the uniform corrosion is especially small at high temperature.

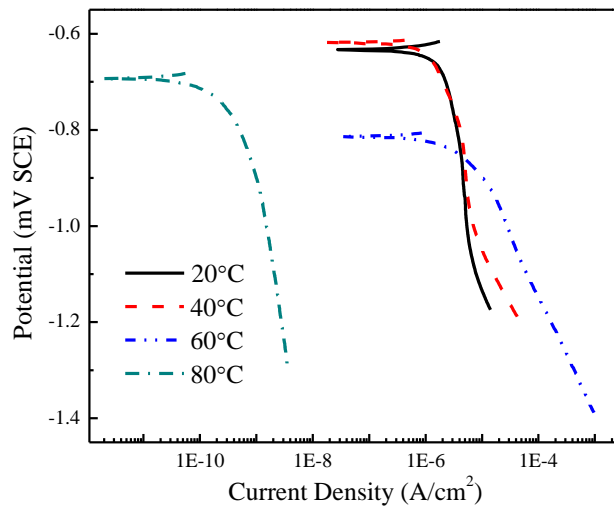


Figure 6 Polarization curve of 2024-T3 alloy in 0.1M NaCl solutions

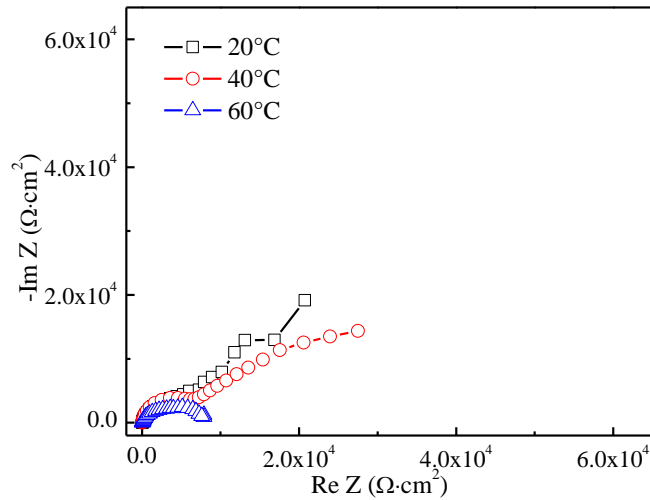


Figure 7 EIS of 2024-T3 alloy in 0.1M NaCl solutions for 24 hour

In Fig. 8 (a) and (b), an apparent difference of surface morphology is shown under low and high temperature exposure. This evidence again supports the results of EIS that corrosion surface is mass transport controlled at low temperature, whereas a dense passive film protects the aluminum surface from corrosion. This film is composed of amorphous aluminum hydroxide, but can be crystallized to polycrystalline in a long term. Cross-sectional images obtained by focused ion beam (FIB) and transmission electron microscopy (TEM) images showing corroded surfaces after immersion at low and high temperatures. This is showing the structure of this passive film is usually two layered consists of a thin oxide layer underneath a thick hydroxide. The thickness of oxide is less than 100 nm, where the thickness of hydroxide is around few hundred nanometers depending on the environment.

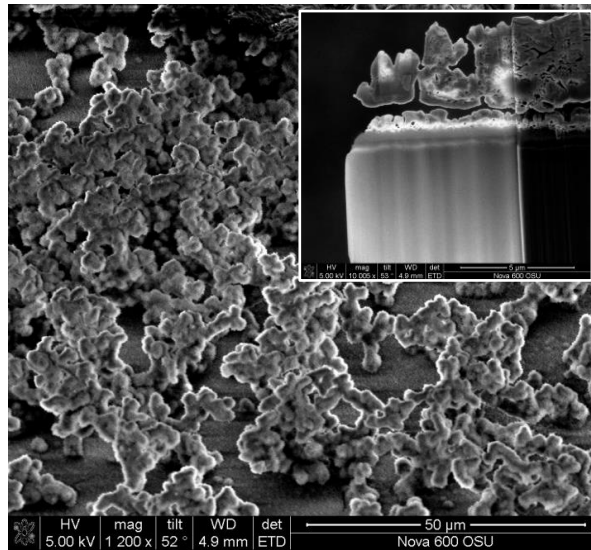


Figure 8(a). SEM of 2024-T3 alloy in 0.1M NaCl at 20°C

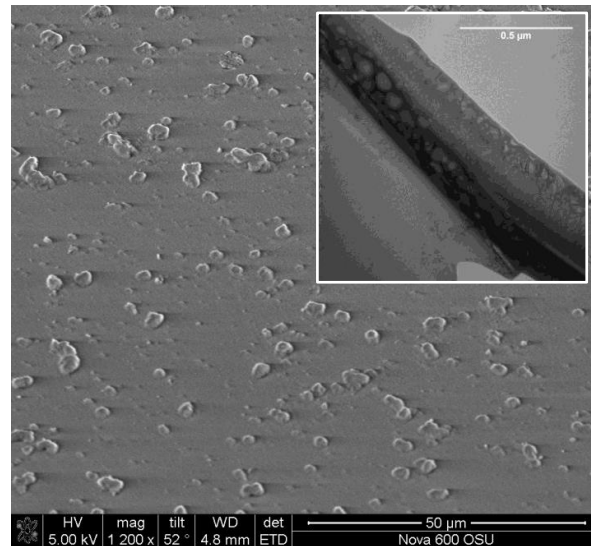


Figure 8(b). SEM of 2024-T3 alloy in 0.1M NaCl at 80°C

In conclusion, uniform corrosion is reported to be a significant issue according to the weight loss experiment, where pitting is a minor fraction proportional to the entire weight loss. Uniform corrosion rate is higher at alkaline and low temperature (20 to 40°C) conditions due to oxygen reduction reaction, where uniform corrosion rate is suppressed at elevated temperature caused by time-dependent passivation and decreasing oxygen solubility. Lower oxygen reduction reaction rate was proved by cathodic polarization tests; where the limiting current density dropped three to four orders as temperature elevated. Also, a concurrent passivation at high

temperature enhances formation of aluminum hydroxide passive film and retards the corrosion rate. Electrochemical impedance spectroscopy result suggested the uniform corrosion to be diffusion controlled at low temperature, while to be capacitor-like surface at high temperature owing to the passive film formation. This passive layer was proved by SEM/TEM images. As reported in this study, the significance of uniform corrosion has been proved by various approaches, and hence emphasizing the importance of uniform corrosion is critical to pit growth kinetics.

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