INTERGRANULAR CORROSION PROTOCOL DEVELOPMENT FOR 7075-T651 EXTRUSION

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Abstract

This paper details the development of a protocol to induce sharp intergranular corrosion in 7075-T651 extruded aluminium alloy.

The final protocol is based on the ASTM Standard G-110 and involves constant immersion within a hole of a solution of 3.5% NaCl and 1.2% H_2O_2 for up to four weeks.

When exposed for the full four weeks, the average corrosion depth found was 1175 μm, the width was 16.3 μm and the resulting length-to-width aspect ratio of 131. The maximum depth produced was 1800 μm.

1 Introduction

As the cost of new aircraft continues to increase, fleet operators are pressured into extending the planned service life of their fleets. In some instances, this results in aircraft being operated well beyond their planned withdrawal date; for example, the Royal Australian Air Force (RAAF) MB326H Macchi jet trainer was expected to be retired from service before 1980[1] however its life was extended to 1985, and some aircraft were still operating in the late 1990s. As aircraft continue to age, the associated cost of corrosion increases. This cost continues to increase until a time that maintenance is no longer viable; it would be cheaper to replace the aircraft than repair it.

As the cost of corrosion continues to increase, newer, cheaper methods for dealing with corrosion need to be developed. The current approach of 'find it and fix it' can lead to the grinding out of even the smallest amount of corrosion [2]. This method can result in unnecessary reduction in the static strength of the structure (due to the removal of materials) [2]. If the corrosion is too severe, the grind-out may be too damaging to the strength limit of the component such that it needs major repair or replacement [3].

New corrosion impact models, such as the Soft Inclusion model for exfoliation [2, 3] and the Equivalent Crack Size model for pitting [4, 5] offer the potential for significantly improved life prediction of components with corrosion present. Using these types of models may allow for other options, not just grind-out, to be investigated, such as leaving the corrosion in place with more regular inspection intervals. Corrosion-related costs can then be reduced, as costly repairs are not taking place.

To ensure the corrosion impact models are robust enough to be certified and used in the field, any laboratory-produced corrosion needs to replicate what is found on the actual aircraft. It also needs to cover a wide range of corrosion sizes to be flexible enough to deal with any corrosion found.

In this instance, a corrosion impact model is being developed for single-layer intergranular corrosion formed in the bore of a fastener hole. To be realistic and representative, the corrosion needs to be grown as long as possible while remaining thin enough to be classed as intergranular corrosion (and not a very deep pit).

Previous methods of corrosion initiation were investigated, such as electrochemical pre-treatment followed by high-humidity storage. However the resulting depths were either not

enough, as in the case of [6] where 100-400 μm deep corrosion was grown in 500 hours, or not quick enough, as in the case of [7] where over 500 μm of corrosion was grown in five months. Other methods include the droplet method employed by [8], which grew 700 μm in 168 hours, and the constant immersion methods used by various ASTM Standards [9, 10].

Due to the nature of where the corrosion is formed, electrochemical methods of initiation were not investigated as the set-up of the electrochemical cell (with the exposed area being inside a hole) would have been too complex.

1.1 Experimental Work Introduction

This paper discusses the development of a protocol to grow sharp intergranular corrosion up to 2 mm deep in 7075-T651 extrusion. The development begins with an initial test of the droplet and constant immersion methods using a 3.5% NaCl solution.

The testing continues using a two-stage constant immersion method with some success. The success was attributed to an increase in oxygen content at the tip of the corrosion, and so hydrogen peroxide was employed (based off ASTM Standard G-110) [9] as an addition to the 3.5% NaCl solution. This was to force oxygen into the corroded area, increasing the tendency for the corrosion to continue along the grain boundary, rather than into the grain body. Finally masking was used to restrict the number of corrosion strikes to just one.

2 Experimental Material

The material used for the work presented in this paper is the wing skin material from an RAAF legacy-era aircraft. It is extruded 7075-T651 aluminium alloy machined down to a thickness of 0.080" (2.032mm).

Due to its extruded thickness, the microstructure of the material is elongated with very thin, long grains. Another feature of the microstructure is the un-recrystallised nature of the grains – they are very small but form a long pancake structure with relatively straight grain

boundaries in the rolling direction. Shown in Fig. 1 is a grain map representing the 7075-T651 material.
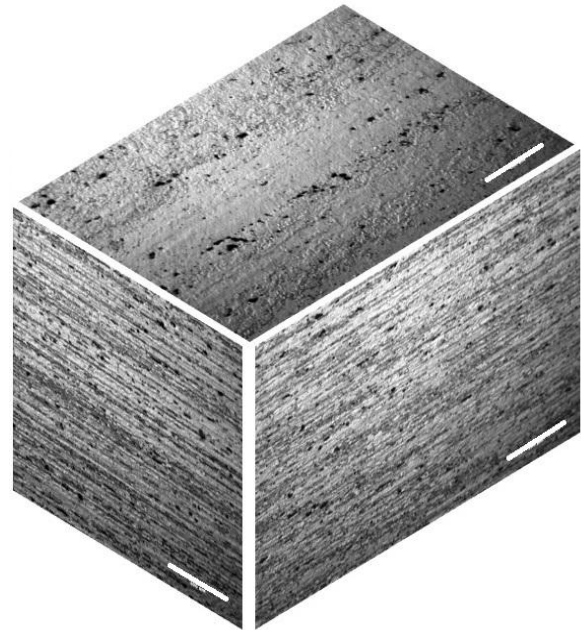

Fig. 1. Grain map of the tested material, 7075-T651 extruded aluminium alloy. The scale bar represents 100μm.

3 Testing of Past Methods

The same coupon geometry was used for all tests described in this paper. The coupons were between 20 and 40 mm long in the rolling direction and approximately 20 mm wide. A ¼" (6.35mm) straight-edged hole was drilled in each sample with a bench drill. The holes were then cleaned with distilled water and ethanol (to remove any swath or oil from inside the hole).

Following exposure to the corrosive medium, each sample was cleaned with distilled water then nitric acid in an ultrasonic bath. The samples were then rinsed in ethanol and dried with hot air.

The samples were then cut and cold mounted on edge in resin. Serial sectioning revealed the corrosion within the sample one layer at a time. This was then imaged and measured for depth and width.

3.1 Constant Immersion in NaCl

The constant immersion method involves sealing one end of the drilled hole with silicone and filling it with the required solution. Once the hole is clean, one end of it is then sealed with a non-reactive silicone (in this case, Permasil 626). The process for doing this begins with filling the hole with BlueTac so it is flush with one side. That side (including the flattened BlueTac) is then covered with silicone and left to dry for 24 hours.

When the silicone is dry, the BlueTac is removed and the hole cleaned with distilled water, acetone and ethanol (on a cotton bud), then dried with a hair dryer. A schematic of the finished product is shown in Fig. 2.
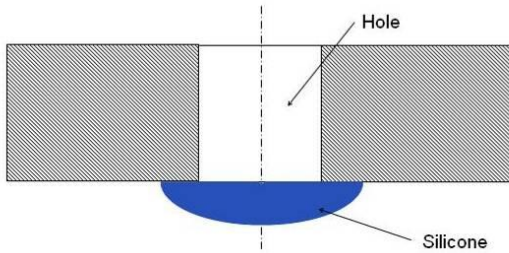

Fig. 2. Schematic of hole-sealing method for corrosion samples.

Approximately 0.1 mL of 3.5% Sodium Chloride (NaCl) solution was placed inside the hole (enough to fill it) and left for three to four weeks at 97% relative humidity (RH). Every week the solution was topped up with distilled water.

This method resulted in more pit-like corrosion than intergranular. The average depth of the resulting corrosion (after three and four weeks exposure respectively) was 105 and 150 μm. The average width was 27 and 37 μm and the average aspect ratio was 4.6 and 6.8. The largest was 365 μm deep, however it was also 40 μm wide. The ideal corrosion will have a length-to-width aspect ratio approaching 100. Overall, for the basic constant immersion method, the largest aspect ratio was 17.

An example of this type of corrosion is shown in Fig. 3.
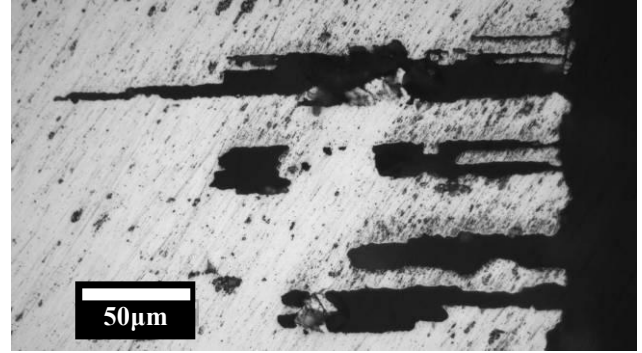

Fig. 3. Example of corrosion found using constant immersion in 3.5% NaCl solution.

To show that this corrosion was intergranular in nature and following the grain boundaries, the sample was etched using Keller's Reagent to reveal the grain structure. Shown in Fig. 4 is the same corrosion as in Fig. 3.
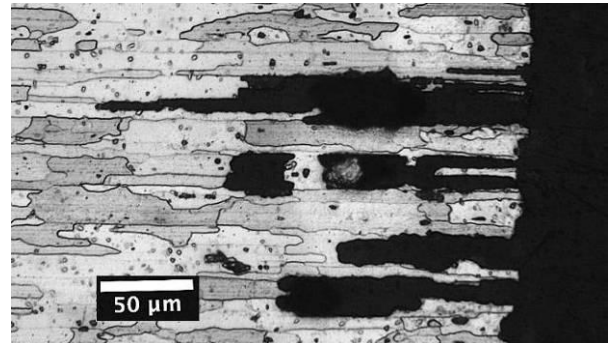

Fig. 4. Etched version of the corrosion found in Fig. 3.

3.2 Droplet of NaCl

The droplet method was based on the work by Knight et al [8], whereby a small droplet (0.002 mL) of a 3.5% NaCl solution was placed on the end grain of a stub of both 2024-T351 and 7050-T7451.

For this paper, a small droplet (approximately 0.005 mL) of 3.5% NaCl solution was placed within the ¼" hole on both the TS and LS orientations of the hole, as shown in Fig. 5. The droplet was refreshed with distilled water every two to three days as, even though it was stored at 97% RH, the droplet still dried out.
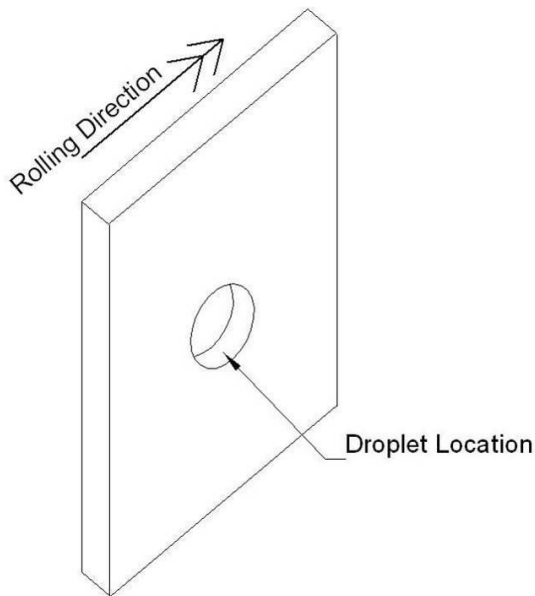
Fig. 5. Location of droplet for LS orientation. Location for TS orientation is 90° to above.

Unfortunately this method did not result in any visible corrosion. As such, this method was disregarded from future work.

4   Adaptation of Constant Immersion Method

As stated in the previous section, the constant immersion method produced corrosion that followed the grain boundary, indicating intergranular corrosion. However, the depth the resulting corrosion reached was too short and the aspect ratio was too low to be useful.

This indicated the corrosion environment was not ideal to produce thin, sharp intergranular corrosion. A number of other tests, based off the initial constant immersion test, were conducted. Most involved a two-stage process aimed at refreshing the solution half way through the four week exposure.

The results of this method appeared to only increase the width of the corrosion found, with the average rising from 37 to 55 µm for the four week exposure. There was little to no increase in the penetration depth found so the average aspect ratio fell to around 3.

One of the new tests involved using the initial constant immersion method for two weeks, then tipping the solution out and rinsing the hole. The sample was then placed back in

97% RH for another two weeks, without re-filling the hole. This resulted in the corrosion forming a number of thin layers from two to three main corrosion sites. This is shown in below in Fig. 6.
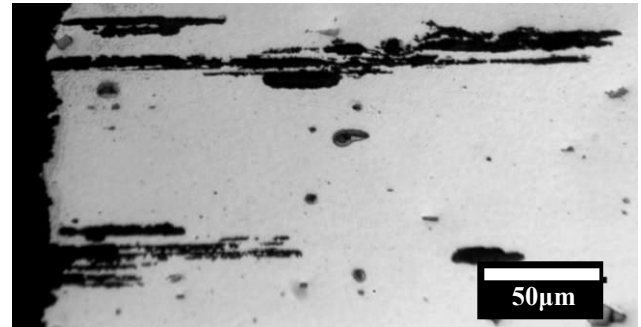

Fig. 6. Layered corrosion found using one adaptation of the initial constant immersion test.

5   The Use of ASTM Standard G-110

The author believed the corrosion found in the previous chapter was a result of an increase in oxygen reaching the corrosion tip. According to Frankel [11], one of the possible cathodes in pitting corrosion is oxygen. When the local pit environment becomes depleted in this, the most cathodic reaction shifts to the "boldly exposed surface" [11]. It is possible to transfer this to intergranular corrosion − as the oxygen is depleted at the corrosion tip (due to corrosion product and a longer path to get to the tip), the reaction shifts to the exposed surface, widening the corrosion.

To test this, ASTM Standard G-110 was investigated as an alternate corrosive medium. ASTM G-110 uses a six hour exposure to a mixture of 1 M NaCl and 0.3% H_2O_2 [9]. These conditions in a constant immersion environment resulted in no visible corrosion.

5.1   Modification to the Solution Concentration and Exposure Time

The next stage of testing utilised a slightly longer exposure time, up to 18 hours, and an increase in the H_2O_2 concentration. One study [12] showed an increase in intergranular attack at peroxide concentrations up to 1.2%.

This stage of testing involved a combination of the original 0.3% and 1.2% concentrations of H_2O_2, the original 1 M NaCl concentration and six and 18 hours of exposure. This produced a number of occurrences of sharp IGC up to 150 µm, one of which is shown in Fig. 7.
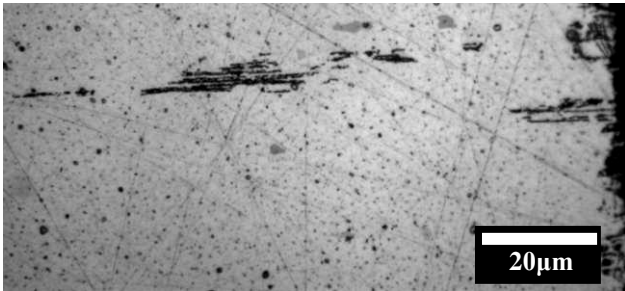

Fig. 7. Example of intergranular corrosion using 1.2% H_2O_2 concentration and 18 hours exposure

Following from the finding above, the exposure time was again increased, this time up to one, two, three and four weeks. As shown above, the largest corrosion was found with a peroxide concentration of 1.2%. For this test, this was again increased to include 2.4% to investigate that effect.

It was also found that after the required time the level of fluid had increased significantly, resulting in some of it overflowing the hole. It was explained that this is due to the saturation concentration of NaCl at 97% RH, which is approximately 0.6M. The solution will draw more water from the high humidity to reach this concentration (by increasing the volume of water, the solution is diluted), thus increasing the level of fluid. For this reason, the rest of the tests were conducted using a 3.5% NaCl solution as this is closer to the 0.6M saturation concentration, limiting the chance of overflow.

The increase in exposure time and concentration resulted in IGC strikes up to 900 µm long in as little as two weeks, as shown in Fig. 8.

Fig. 8. Example of IGC using 3.5% NaCl, 1.2% H_2O_2 solution exposed for two weeks.

As can be seen from above, a number of corrosion strikes were found through the thickness. To accurately replicate real-life corrosion, only one or two main strikes (or layers) should be present. As such, a method for controlling the exposed area was developed.

6.1 Masking of Samples

To combat the issue of a number of corrosion strikes within the thickness, various methods of masking were investigated. The simplest method available was to use a masking lacquer inside the hole and remove a thin ring around the hole, exposing that area. In this instance, Vishay's Barrier J II was available.

For this test, a metal scalpel was used to create the exposure ring in the hole. This had the added effect of marking the underlying metal, allowing identification of the exposed area during sectioning (to determine if the corrosion was growing from the scalpel mark or elsewhere).

The lacquer was carefully applied around the hole, on the top surface of the sample and down onto the silicone. This was left to dry for 24 hours. Once the exposure ring was made, the samples were exposed using the same combination as before – 1.2% and 2.4% H_2O_2 for one, two, three and four weeks.

For the samples exposed to a lower concentration, this method constrained the corrosion to a single layer, initiating from where the scrape was. The higher concentration of peroxide appeared to break down the lacquer

and initiated multiple corrosion strikes along the thickness.

As the hydrogen peroxide in the solution would break down within a few days, replenishment of the peroxide was necessary. Half the samples had the whole solution replaced every two days – this also resulted in the lacquer breaking down (even with a lower concentration of peroxide). The rest of the samples only had the peroxide replaced, resulting in little breakdown of the lacquer.
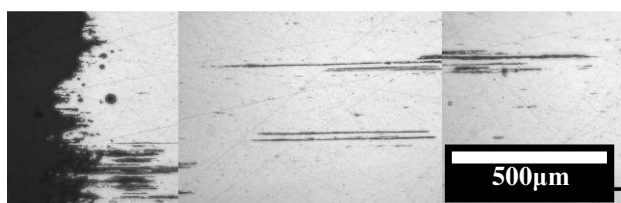
Figs. 9 and 10 show examples of the corrosion made.

Fig. 9. Example of corrosion found using masking method described above. 1500 μm were grown from three weeks exposure to a higher H_2O_2 concentration. The higher concentration lead to a breakdown in the masking lacquer, resulting in the second, lower corrosion strike.
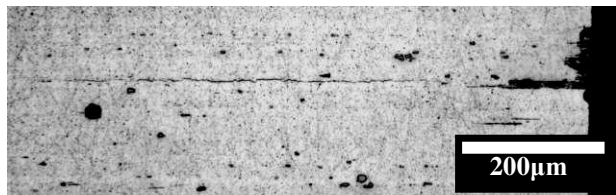

Fig. 10. Example of corrosion found using masking method described above. 700 μm were grown from two weeks exposure.

once a week, but it only needed 5-10 μL). This resulted in 1800 μm of corrosion and is shown in Fig. 12.

7 Aspect Ratio Progression

This final section presents a graph of the aspect ratio progression throughout the process of modifying ASTM Standard G-110. As can be seen in the figure below, for each test configuration the aspect ratio continues to grow.

Fig. 11, below, shows all the results of the following tests:

1. Basic constant immersion of 3.5% NaCl solution
2. Two-stage constant immersion of 3.5% NaCl solution
3. Modified, un-masked test based off ASTM G-110
4. Modified, masked ASTM G-110 test

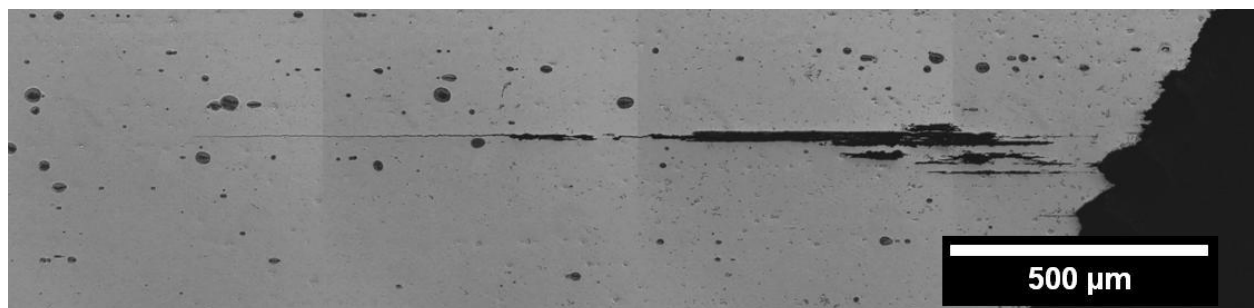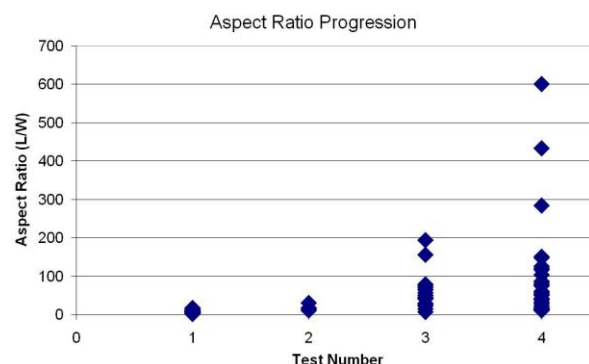Fig. 11. Graph of aspect ratio (L/W) progression during the modification process.

Fig. 12. Example of corrosion in best case using the modified ASTM Standard G-110.

The best case found was exposed for four weeks with a solution of 1.2% H_2O_2. Only the peroxide was replenished every two days, with top-up of the solution if needed (approximately

Table 1 shows an expansion of Test Number 4 from above. This shows the aspect ratio changes as the exposure weeks progress from one through to four weeks.

Table 1. Exposure time versus average dimensions of resultant corrosion using final corrosion protocol

Exposure Time (weeks)	Depth (μm)	Width (μm)	Aspect Ratio (L/W)
1	550	8.3	62
2	580	9.7	110
3	702	17.7	116
4	1175	16.3	131

8   Conclusions

The aim of this work was to determine the fastest method to induce long, sharp intergranular corrosion from the bore of a hole in 7075-T651 extruded aluminium alloy. Through a series of experiments it was found that modifying the conditions of ASTM Standard G-110 resulted in corrosion up to 1800 μm deep with a width of 10 μm.

The final method that gave the most realistic representation of in-service corrosion involved a four week exposure of a masked hole to a solution of 3.5% NaCl and 1.2% H_2O_2. This gave an average depth of 1175 μm, an average width of 16.3 μm and a resulting length-to-width aspect ratio of 131. These measurements fall within the ideal range for further testing.

8   Acknowledgements

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