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Contractor Report

PITTING PROTOCOL

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Introduction of corrosion pit

The corrosion pit is introduced into the specimen after machining. The specimen dimensions are given in Figure 1. The procedure involves selective masking and subsequent corrosion in an acid bath with an applied corrosion current. Pit uniformity is achieved by controlling the masked area dimensions, current density, and corrosion time. When the protocol below is followed, users will attain consistent pit depth, length and diameter across all specimens of similar geometry. This pitting protocol was successfully tested on the AA 7475 and AA 7075-T651 alloys.

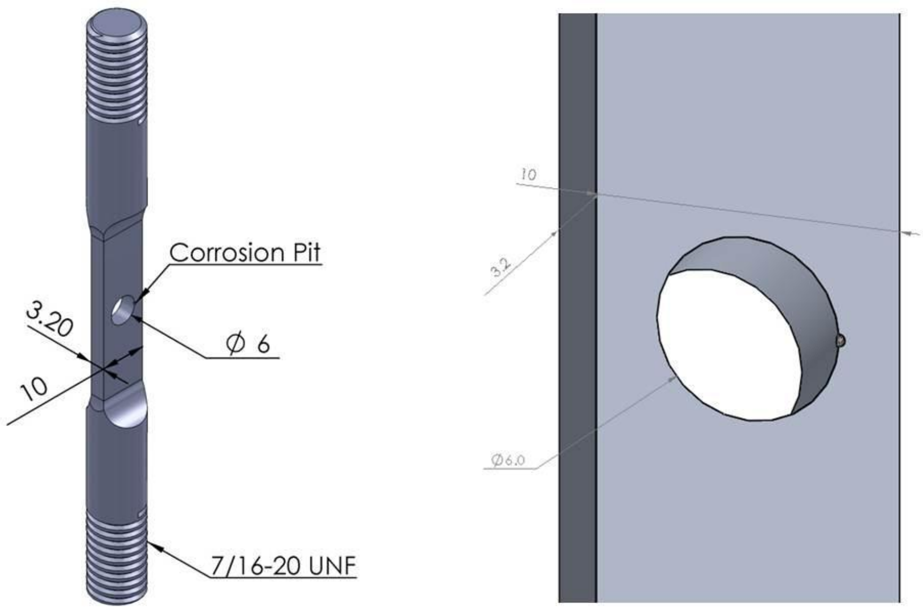

Figure 1. Specimen geometry with dimensions. All dimensions are given in millimeters (mm).

Pitting current magnitude and duration

The size (volume) of the corrosion pit is directly proportional to the mass dissolved from the material due to the applied corrosion current. For constant corrosion current the mass loss is calculated using Faraday's Law:

$$m = \frac{ItM}{zF} \tag{1}$$

where m is mass in grams, I is current in Amperes, t is time in seconds, M is the molar mass in grams/mol, z is the number of electrons exchanged per ion, and F is Faraday's constant (96485 coulombs/mol). The quantity M/z, called the equivalent weight, is calculated as 9.55 grams for AA 7075. The relevant numbers are inserted in the above equation (1) and the pitting duration 't' is calculated.

$$t = \frac{mF}{I}\frac{z}{M} = \frac{\mathrm{m}.96485}{I}\frac{1}{9.55} \tag{2}$$

Constant current is set by the user, leaving mass as the only unknown. The mass of the corrosion pit is calculated by considering the volume of the pit and density of the alloy. The corrosion pit is a quasi-spherical flaw located on an edge of the specimen center hole. However, volume of the pit is calculated by assuming a spherical corrosion pit.

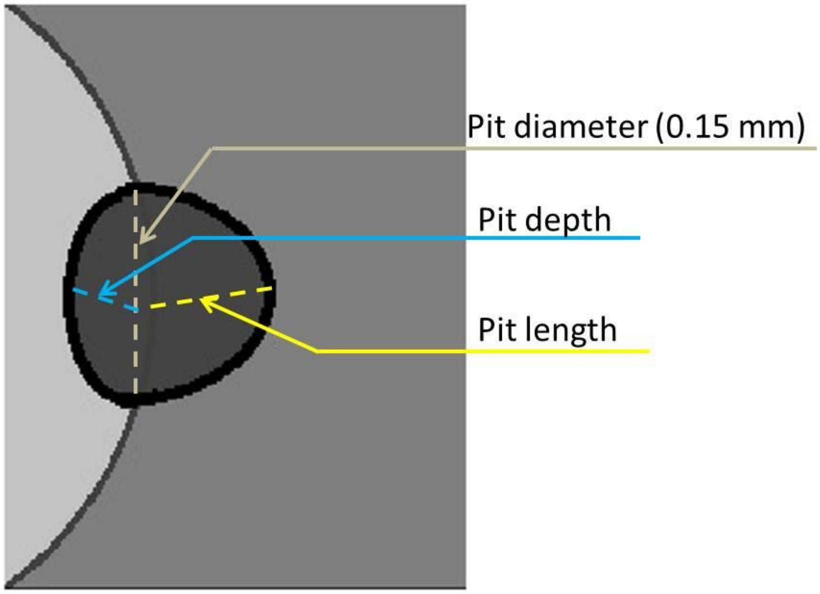

Figure 2. Schematic diagram of the corrosion pit with dimensions.

Figure 2 shows the schematic diagram of the corrosion pit at the edge of specimen center hole. The corrosion pit diameter, pit length and pit depth dimensions are labeled in the figure. The volume of the corrosion pit with radius 0.075 mm, when 0.15 mm tape hole is used, is much smaller than the radius of the center hole (3 mm) of the specimen. Therefore the corrosion pit is assumed to be placed at the edge of a flat rectangular bar. The volume of the corrosion pit is exactly ¼ of the volume of the sphere:

$$V_p = \frac{1}{4}V_s = \frac{1}{4} \times \frac{4}{3}\pi r_{pit}^3 = \frac{1}{3}\pi r_{pit}^3 \quad (3)$$

where V_p is the volume of the pit, V_s is the volume of the sphere and r_{pit} is the radius of the pit. For a pit of 0.075 mm radius, the volume equals 4.42 x 10^{-7} cm^3. The density of AA 7075 is 2.81 grams/cm^3, so the mass of the corrosion pit is 12.42 x 10^{-7} grams. Therefore:

$$t = \frac{12.42 \text{ x } 10^{-7} \times 96485}{I}\frac{1}{9.55} \quad (4)$$

Table 1 gives the list of pitting times and current densities for different pit sizes for AA 7075. Since the pit size (and mass) is proportional to the radius to the third power, significant time increases are required for larger pits.

Table 1. Pitting times and current densities for different pit sizes for AA 7075

Applied current (A)	I = 0.0002		
Drill bit diameter (mm)	0.10	0.15	0.20
Pit radius (mm)	0.050	0.075	0.10
Pitting time (sec)	18.6	62.7	148.6
Current Density (A/cm^2)	2.55	1.13	0.64

The current-based pitting calculations assume that the applied current is constant. Therefore, it is critical to maintain a steady corrosion current by providing a clean corrosion surface and using an adequate power supply that can quickly change the applied voltage to maintain a constant current. Multimeters provide an optimal source of power and are useful for controlled current or voltage operations. Multimeter is better than a simple DC power source for this protocol because the voltage variation during the pitting process needs to be monitored to avoid overvoltage situations.

Automatic removal of bubble formation
The electrochemical reactions of the pitting process produce hydrogen bubbles at the corrosion site. For small pit diameters, the corrosion site can be totally obscured by the bubble in a few seconds or less. These bubbles must be removed for the corrosion reaction to proceed in a predictable way. This process is shown in the setup in Figure 3.

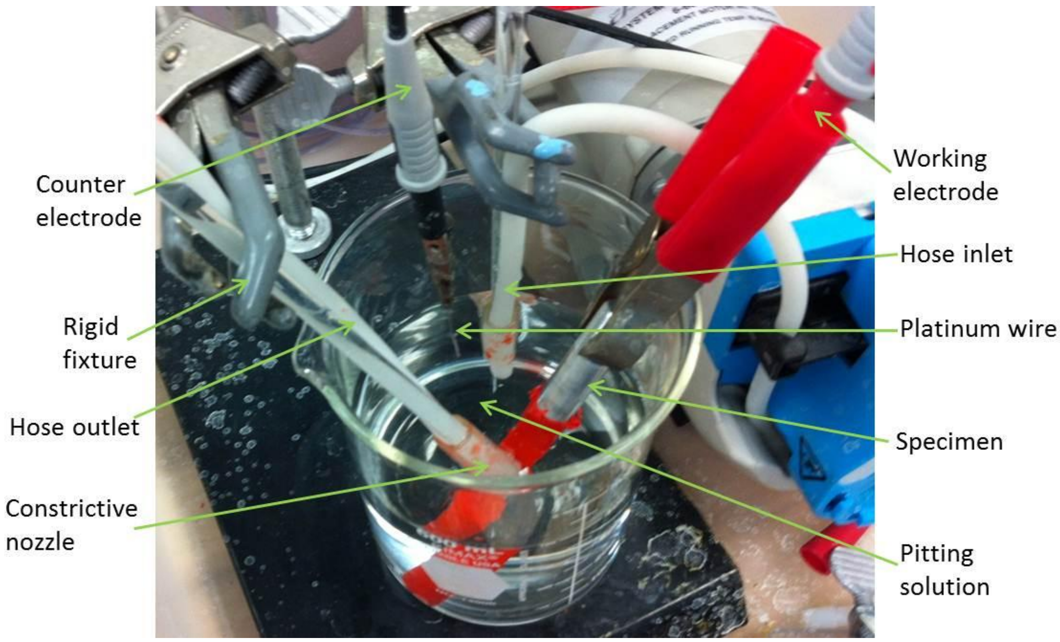

Figure 3. Corrosion pitting setup using forced solution circulation.

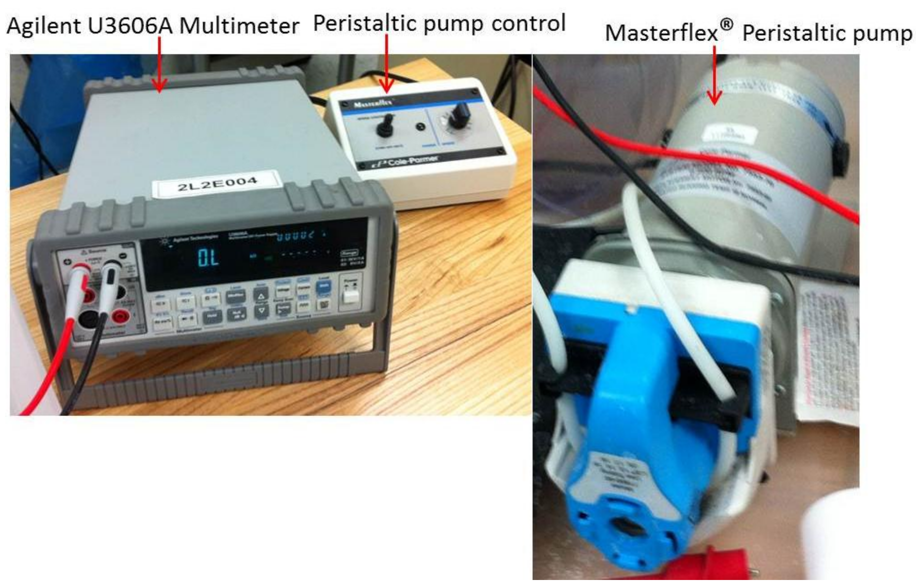

Figure 4. Agilent U3606A multimeter, Masterflex® peristaltic pump and pump controller.

The specimen is placed in the beaker containing the pitting solution and is connected to the positive terminal of the power source by means of an alligator clip. A constrictive nozzle (see Figure 3) with a 1/16 inch inner diameter is coupled to the hose outlet to propel the liquid near the corrosion pit. The nozzle is aimed at the target corrosion site using a rigid fixture. With sufficiently high flow rate (> 200 ml/min – dial setting 5 on the pump controller) gas bubble buildup near the corrosion pit is completely prevented. Since the masked tape hole is 150 µm in diameter, mass transfer of ions to and from the exposed metal surface can limit the corrosion kinetics. In a non-circulating liquid, the transfer of ions to and from the corrosion site constitutes the mass transfer rate limitation for the corrosion process. The circulation of pitting solution eliminates this mass transport rate limitation. In the present setup, the circulating liquid enhances the ability to control the corrosion rate with constant applied current. A peristaltic pump circulates the pitting solution around the specimen to minimize bubble formation. Figure 4 shows the Agilent U3606A multimeter that is used to supply constant current, Masterflex® peristaltic pump and pump controller to circulate the pitting solution on to the specimen at a required flow rate.

Detailed Pitting Procedure

A tape with a desired hole dimensions is placed at the center of one edge of the hole in the specimen in a such a way that a portion of the metal on the flat surface and along the hole surface are visible through the tape hole. Prior to drilling the tape holes, score the tape into small sections 2 mm by 10 mm. Drill the hole at the center of each small tape section using a 0.20 mm or 0.15 mm drill bit. About 25 slow rotations of the drill bit held by the drill vise will yield a clean hole through the tape without leaving behind any tape debris or residue.

Transfer the tape to the specimen by means of two tweezers, centering the hole in the tape on the edge of the specimen hole. Ensure that the tape is placed at the center of specimen hole along the length (net section in the width direction) of the specimen. If unsuccessful on the first try, the specimen needs to be cleaned thoroughly and a new tape needs to be used. The specimen may be cleaned with isopropanol using a cotton swab. Firmly push down on the tape to ensure complete adhesion of tape to the sample.

Once the tape is properly placed, the rest of the sample should be coated with stop-off lacquer and allowed to dry. Make sure there are no holes or gaps in the paint and that the drilled hole in the tape is not covered by lacquer. More than one coat may be needed in spots. One end of the specimen can be left without coating. This end will serve as the anode grip when connected to the multimeter. It is important to coat the specimen that is in the solution with stop off lacquer to prevent the entire specimen from corrosion except at the hole in the tape.

To pit the specimen, place the specimen in a beaker with the acid solution with the uncoated end at the top. Clip the working electrode (red wire) to the uncoated end of the specimen. Attach the counter electrode to the platinum wire (black wire) and place into the acid. Ensure that the anode clip is not touching the liquid. Start the peristaltic pump and set the speed dial to 5. Make sure that one end of the pump is directed on top of the tape hole. Apply a constant current of 0.2 mA to the sample using an Agilent U3606A Multimeter. Apply the current for 5 minutes, which should be enough to form a pit of about 150 µm in diameter. Monitor the voltage variation during the pitting process. The voltage should be either stable or increase slowly. Typically, the voltage stays in the range of 0.0 to 2.0 V. The voltage sometimes can rise quickly; rate of increase can be between 10 to 20 mV per second. The quick increase in voltage indicates that the circuit resistance is high as a result of the tape hole being masked. In such a case, the experiment should be stopped and the tape placement procedure on the specimen needs to be re-done. After pitting, the specimen is rinsed with water and the hole in the masking tape is checked to ensure corrosion has occurred. The hole should be dark which is an indication of corrosion product build-up. If not, redo the experiment. After successful pitting, the tape and lacquer is removed. Clean the specimen with isopropanol in an ultrasonic cleaner for 15 minutes to remove any debris from the pit.

Supplies and Step-wise Pitting Procedure

This procedure is used to create corrosion pits of 250 µm or less in diameter in AA 7075 specimens. The pitting solution was designed for aluminum alloys. The target size of the pit is controlled by the size of the drill bit, the applied corrosion current and duration of the applied corrosion current.

Required Supplies

- DC Power Supply (Agilent U3606A Multimeter)

- Two wires with alligator clips (standard size alligator clip for platinum wire and large size clip to hold 10 mm diameter specimen)
- Platinum wire for counter electrode (1 mm diameter)
- 400 mL beaker for pitting solution bath
- Teflon sheet (6″×6″×1/16″)
- 0.15 mm diameter (High Strength Steel) drill bits
- Drill bit vise (STR 166A Pin Vise 0-1 mm)
- Smart Stripe Tape (4.2 mils thick), 3M 471 Vinyl Tape (5.3 mils thick)
- Tweezers (2) (12 cm length and broad tip stainless steel tweezers)
- Micro Super XP 2000 Stop-off lacquer
- Razor blade
- Isopropyl alcohol
- Branson B5510 Ultrasonic cleaner (Tank size: 11.5″×9.5″×6″, Capacity: 2 ½ gallon)
- Pitting Solution
  0.1 M $AlCl_3$ + 0.86 M NaCl with HCl added to make the pH 2
    - Mix 50.25g NaCl and 13.34 g Anhydrous $AlCl_3$* (or 25 g hydrated $AlCl_3$) in 1 L of pure H_2O
    - Add HCl until pH = 2
      **Note: Anhydrous $AlCl_3$ reacts violently with water. Consult MSDS.*

- Masterflex® Peristaltic pump
  - 3 feet hose, size L/S 16 (1/8 inch inner diameter, ¼ inch outer diameter) (L/S stands for Laboratory Science, a registered trademark of Masterflex®)
  - Nozzle with inner diameter less than 1/16 inch
- Fixtures to hold the inlet and outlet hoses

Step-wise Pitting Procedure:

1. Make the pitting mask
   a. Place some Smart Stripe tape on the Teflon sheet
   b. Score the tape into 2 mm x 10 mm rectangular strips using a razor blade
   c. Place the drill bit inside the drill bit vise and grip the bit by tightening the vise
   d. Gently drill a hole in the center of each rectangle, through the tape and Teflon sheet by applying minimum pressure
      a. 25 rotations will be sufficient to form a neat hole in the tape without forming any tape debris
   e. Use a microscope (Olympus SZH microscope) to check that the hole on both sides is perfectly circular and free of debris, as shown in the Figure 5 below

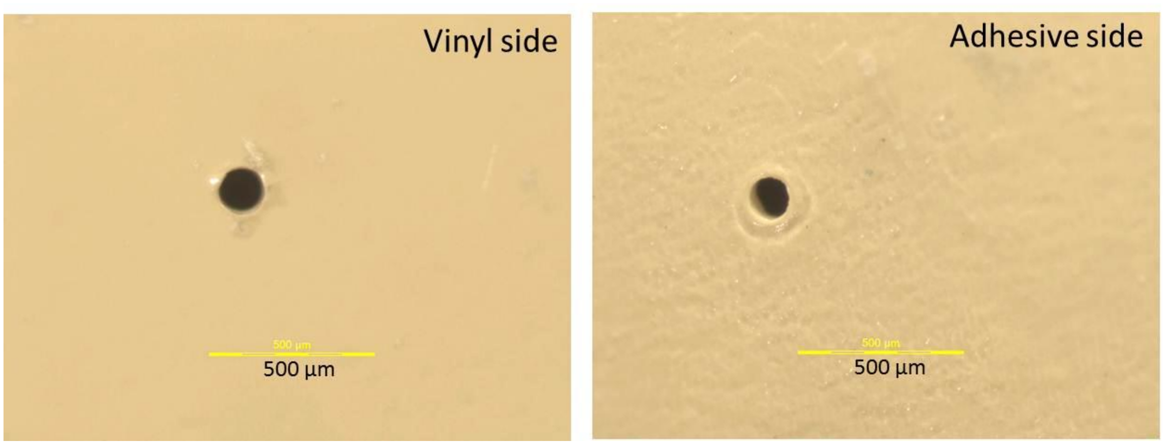

Figure 5. Tape hole (0.15 mm) on smart stripe tape viewed from both sides.

2. Transfer the tape to the specimen
    a. Peel the tape with hole off Teflon sheet using two tweezers
    b. Hold the specimen at an angle under the microscope using a stand and holder (see Figure 6 below)

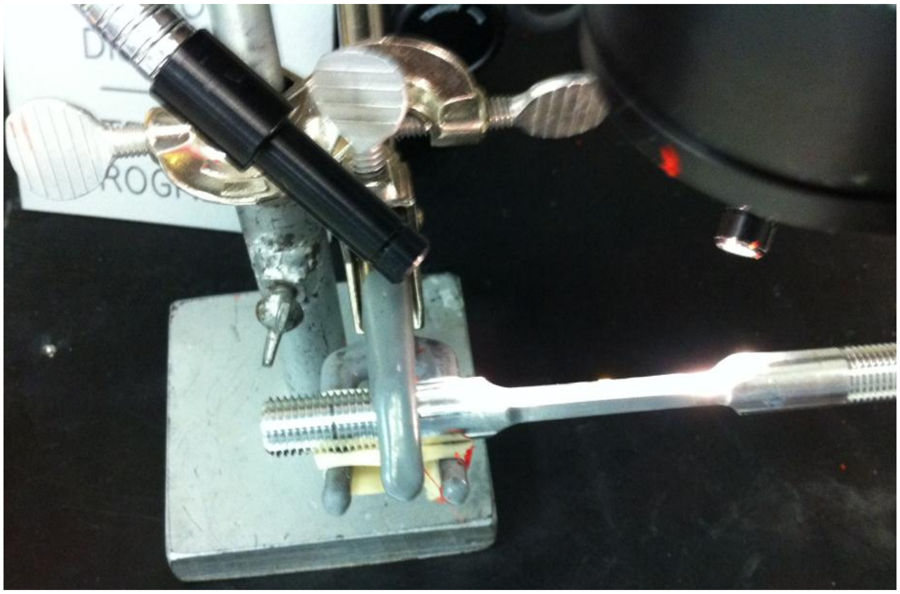

Figure 6. Stand setup under the microscope to hold the specimen.

    c. Centering the hole in the tape at one edge of the specimen hole is done by the use of two tweezers. Accurate positioning is critical
        a. If unsuccessful on the 1st try, a thorough cleaning of the specimen and new piece of tape may be necessary since the tape adhesive tends to leave an adhesive residue on the specimen
    d. Push down on the tape firmly with the tweezers and hold for about 10 seconds to ensure 100% adhesion of tape portion near the hole
    e. The remaining portion of the tape which is away from the hole is pressed with tweezers so that the tape is completely wound around the edge of the center hole of specimen.
    f. Ensure that the tape adhesive does not seep through the tape and cloud the specimen Below (Figure 7) is an image of a good placement of the tape at the edge of the specimen center hole. Ideally, equal portions of the metal on either surface should be visible through the tape hole
    g. Proper placement of the tape hole at one edge of the specimen center hole is critical. Ensure that the tape hole is centered along the middle of the specimen center hole

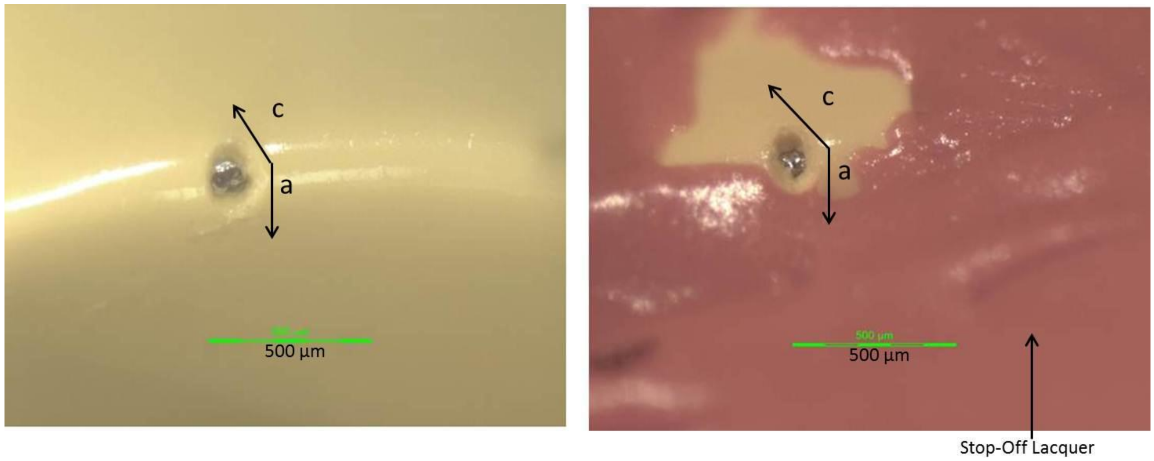

Figure 7. Tape placement along the specimen hole edge.

3. Paint the specimen with stop-off lacquer and let dry for at least an hour
    a. Inspect the specimen after drying to ensure that the specimen is fully coated
    b. Fill up any holes or gaps in the paint by applying additional lacquer and let dry for about half hour (small amounts of lacquer dry quickly)
4. Setup the corrosion reaction
    a. Prepare the liquid circulation hose and pump
    b. Pour the pitting solution into the 400 mL beaker
    c. Place the masked portion of the specimen in the solution
    d. Hold the specimen at an angle in the beaker
    e. Direct and fix the hose outlet nozzle tip so that the nozzle is directly above the tape hole; the nozzle can rest on the specimen (see Figure 3 above)
    f. Direct and fix the hose inlet so that it is fully immersed in the solution
    g. Clip the positive electrode to the specimen (working electrode)
    h. Clip the negative electrode to the platinum wire (counter electrode)
        a. Ensure that the clips are not touching the liquid (firstly, to ensure that only the metal through the tape hole is exposed to the pitting solution thereby the pitting time relates to the corrosion of the metal at the specific location and secondly, to avoid corrosion of the clips and damage them)
    i. Engage the peristaltic pump, at 200 mL/min
        a. 200 mL/min is dial setting 5 on the 600 rpm Masterflex® pump with L/S® 16 hose
5. Apply the corrosion current
    a. Set the applied current to 0.2 mA
    b. Use constant current (CC) mode in the Agilent U3606A Multimeter
    c. Press the ‘OUT/STBY’ button on the multimeter to start the experiment
    d. Monitor the voltage variation during the pitting process. An overvoltage condition (steep rise in the voltage with time, e.g., 10 to 20 mV per second) may occur if the connections are not properly made, or if a gas bubble blocks the tape hole
    e. Run the current for 5 minutes. This should yield a pit of roughly 150 µm in diameter
6. Stop the current by pressing the ‘OUT/STBY’ button on the multimeter
7. Stop the pump
8. Disconnect the specimen from the alligator clip
9. Rinse the specimen with water
10. Observe the specimen under the microscope to ensure that corrosion did occur
    a. The tape hole region looks dark due to corrosion product which indicates a pit did form
11. Remove masking and clean the pit region with isopropanol using a cotton swab
12. Ultrasonically clean the specimen in isopropyl alcohol for 15 minutes
13. Collect the pitting solution and store it for later use. The pitting solution is re-used for every pitting experiment

Figure 8 shows an example of pits that were formed by following the above procedure. The pits are less than 250 µm in diameter. With careful placement of the tape, smaller pits can be achieved using the 0.15 mm drill hole in the tape.

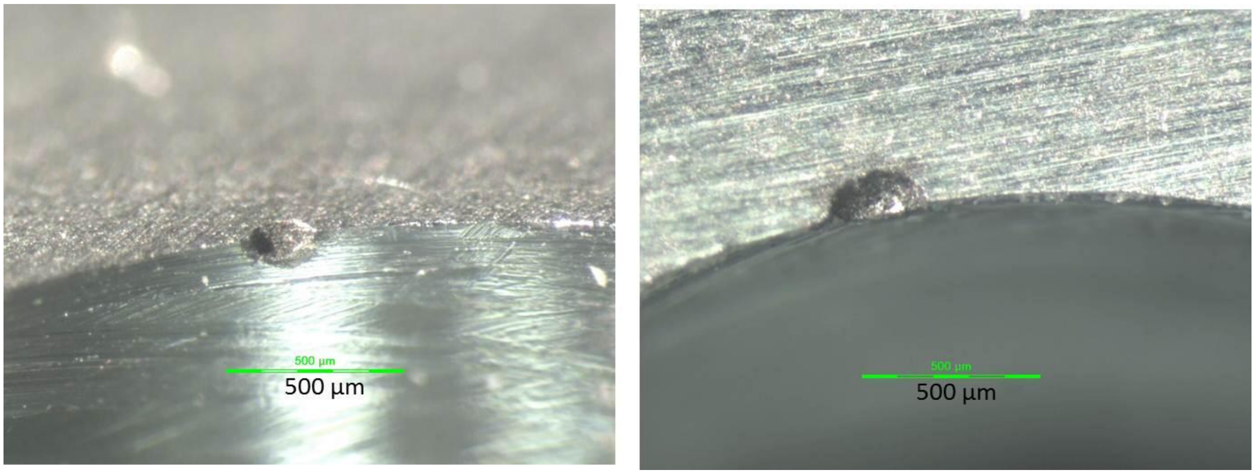

Figure 8. Specimens with pits less than 250 µm in diameter.