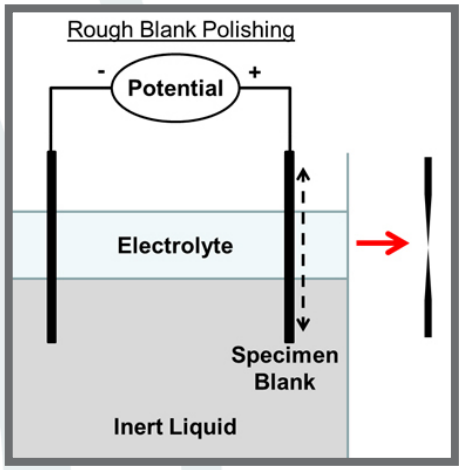
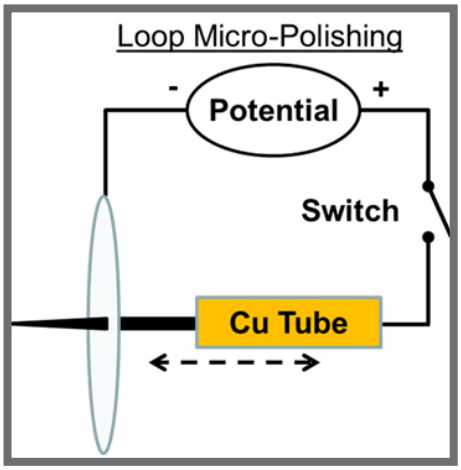



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## Technical Note TN-07 Electropolishing

# APT Specimen preparation: Electropolishing

Electropolishing to make a sharp atom probe specimen involves the reaction of a conductive specimen with an electrolyte under the influence of an electric driving force. This process often requires fine control over various parameters like the active electrolyte, the solvent, electrolyte concentration, solution viscosity, magnitude of voltage, and voltage type (DC, AC or pulse), temperature, and the condition of specimen surface. Although not all of the aforementioned parameters can be rigorously controlled, there may be specific conditions for which their control may be critical for producing sharp and robust APT specimens.

# PROCESS OVERVIEW

The electropolishing step described here is a standard two-step procedure. The first step involves aggressive removal of the specimen shank with a more concentrated electropolishing solution from a beaker. This process involves necking and breaking off the lower half of the specimen or stopping the electropolishing step when the desired shank angle and tip radius is achieved. The second step involves sharpening the tip to its final APT-ready radius by using a relatively dilute electropolishing solution. Depending on the type of starting specimen material and especially its radial dimensions, the average time to produce an atom probe-ready specimen varies from 10 to 60 minutes.

# APPARATUS and SETUP

Vertical and horizontal setups are proposed to conduct rough/high rate and fine/well-controlled electropolishing. The vertical setup may involve using a two layer method for controlling the position of a neck in the middle of the specimen (Figure 1). The horizontal method consists a specimen loading slot and a loop that carries the electropolishing solution connected through a circuit (Figure 2). The horizontal e-polishing setup is generally attached to an optical microscope which allows the user to track the progress of tip-shaping. Depending upon how large the starting sample is and the availability of equipment, both steps could be done in either the horizontal method or vertical method.

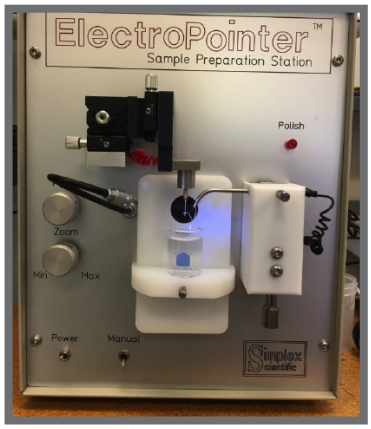



Fig. 1: Simplex ElectroPointerTM for first step rough polishing

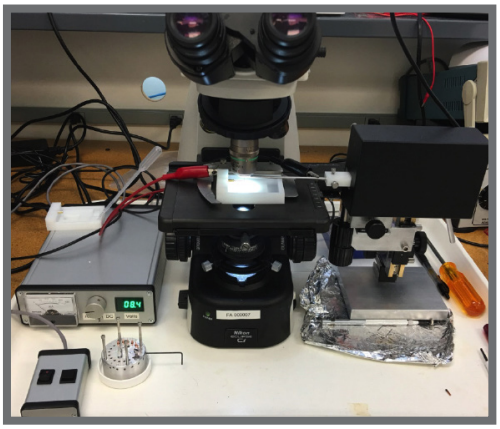


Fig. 2: Simplex manual ElectroPointer for final specimen tuning


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# STEP-BY-STEP PROCEDURE

## Notes on electropolishing

**Safety Considerations:** Electropolishing and chemical polishing require the use of solutions that can be corrosive, poisonous or potentially explosive and it is vital that appropriate occupational health and safety measures are used. It is strongly advised that, prior to working with dangerous chemicals, the individual undertake an appropriate safety-training course. The activity of conducting electropolishing must abide by the risk assessments and safe standard-operating procedures, consistent with the regulations of the laboratory, institution and country in which the work is being undertaken, and use proper personal protective equipment (PPE) at all times.

## 1 Preparation of starting blank

The starting blank (sometimes called a matchstick) ideally possesses a square/circular/symmetric cross section to avoid non-uniformities in the final tip shape. Such a cross section can be obtained by careful cutting of the parent metal sheet/block using a diamond saw, wire saw, or by other means like Electric Discharge Machining (EDM).

**Note:** Cutting the matchstick not be necessary if the starting specimen is already a thin wire or has been previously polished for APT.

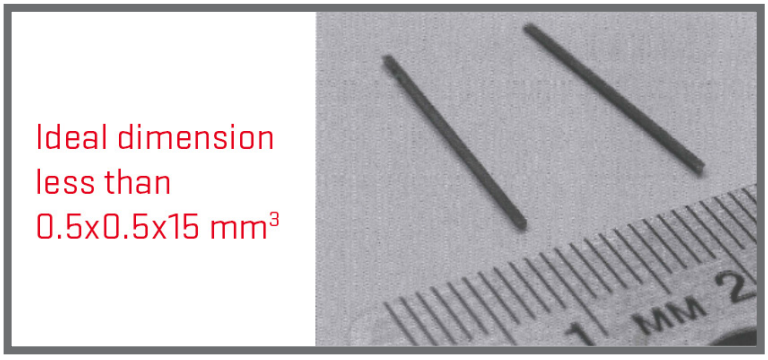



Fig. 3: Example of metal blanks with typical dimensions used for e-polishing.

## 2 Edge cleanup

Mechanical cutting can cause rough edges as shown in Figure 4a, which should be smoothed out by grinding between two pieces of sandpaper (Figure 4b) to avoid the cross-section being non-symmetric.

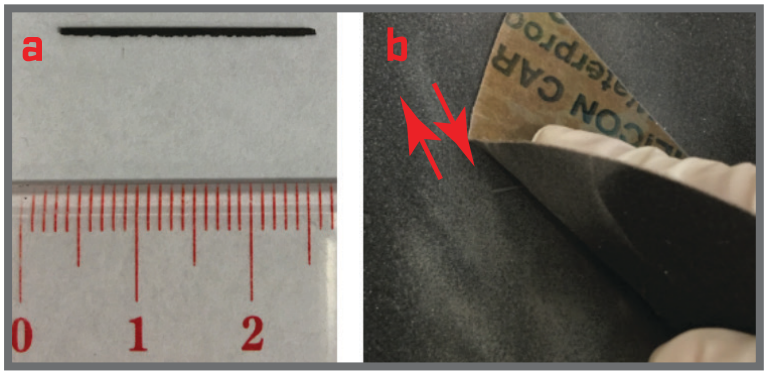



Fig. 4: a) Blank with irregular edges cut by EDM. b) rolling the blank between two pieces of sandpaper to smooth out the edges.

## 3 Electropolishing efficiently

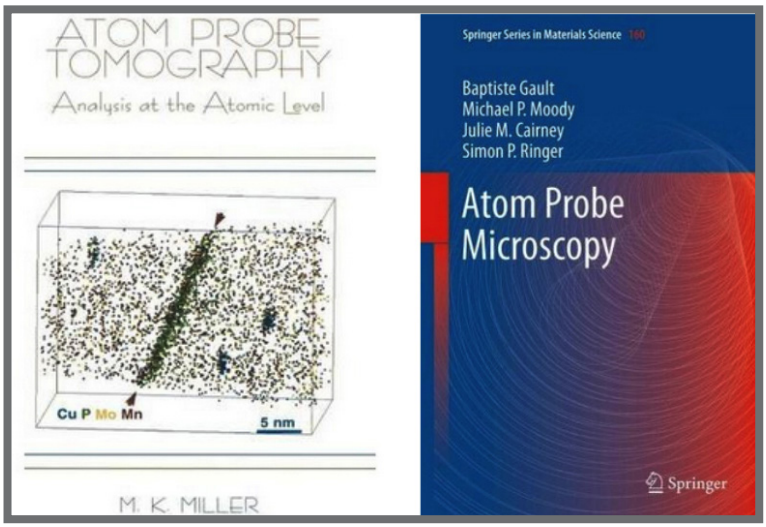
A two-step process is often employed for larger diameter specimens. In a first "rough polishing" step, the blank is polished until the circumference of the blank is significantly lowered or a "neck" forms. "Fine polishing" is then used to sharpen the tip to its final dimensions.

Vertical electropolishing and horizontal electropolishing are the two commonly used setups to conduct the above mentioned "rough polishing" and "fine polishing" which will be conducted using the setups shown in Figure 1 and Figure 2.

# STEP-BY-STEP PROCEDURE

## 4 Electrolyte selection and polishing conditions

Depending on the material system under investigation, the choice of electrolyte varies. An exhaustive list of appropriate electrolytes and conditions to be employed can be found in the atom probe text books, e.g. "Atom Probe Field Ion Microscopy" by Miller et. al. and "Atom Probe Microscopy" by Gault et. al.




## 5 Some commonly used electrolytes

| Materials | Electrolyte | Conditions |
|---|---|---|
| "Universal" Iron-based<br>Nickel-based<br>Aluminum | a) 10% perchloric acid (CAS #7601-90-3) in glacial acetic acid (CAS #64-19-7)<br>b) 2-5% perchloric acid (CAS #7601-90-3) in 2-butoxyethanol (CAS #111-76-2) | 30 V DC |
| Tungsten, Aluminum<br>Molybdenum | 5 wt.% NaOH (CAS #1310-73-2) or KOH (CAS #1310-58-3) in water | 1-10V AC |
| Copper alloys | 70% orthophosphoric acid (CAS # 7664-38-2) in water | 1-10 V DC |

## 6 Blank specimen loading

Crimp specimen blank in Cu stub for easy handling.

Cu stub part numbers:

PN #21609 ID 0.4 mm OD 1.8mm

PN #22933 ID 1.0 mm OD 1.8mm

PN #21610 ID 1.4 mm OD 1.8mm

Crimping can be accomplished using the concentric crimping station CAMECA supplied PN 25742, or with common pliers.

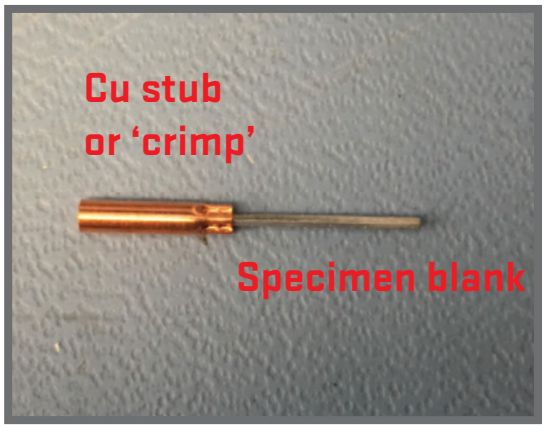



Fig. 5: Ready to polish specimen blank crimped in a large ID (PN #21610) Cu stub.

# STEP-BY-STEP PROCEDURE

## 7 Simplex vertical ElectroPointer

A suitable electropolishing solution required for the initial polishing step is placed in a 10 ml beaker and positioned on the stage below the blank.

Figure 6 is an overview of the vertical electropolishing setup from Simplex.

Figure 7 is a close-up view of the setup in place for operation.

Refer to the 'Installation and operations Guide' from Simplex for startup alignment.

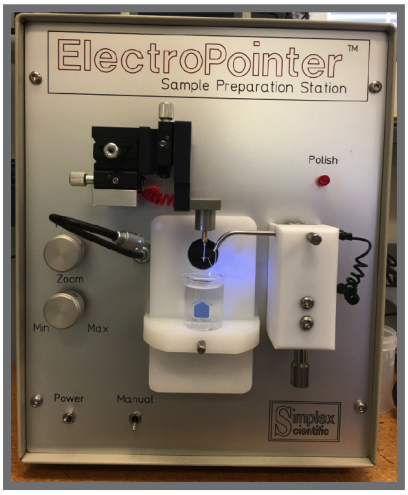



Fig. 6: Vertical electropolishing setup from Simplex.

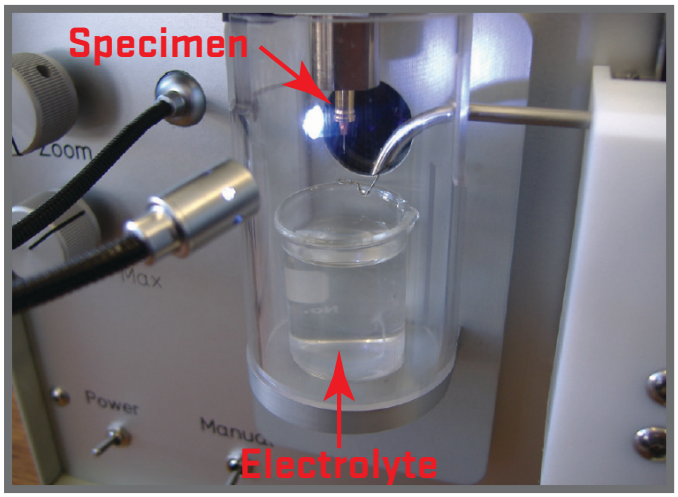



Fig. 7: A close-up view of blank in place for operation.

## 8 Necking

Set the up-down motion on counter electrode accordingly to form a neck in the center of the blank.

Refer to the 'Installation and operations Guide' from Simplex for software operation.

Figure 8 shows a neck being formed on a superalloy specimen using the Simplex EPointer. The necked region is gradually thinned and ready to break into the blank into two tips (Figure 9).




Fig. 8: Preliminary electropolishing. A neck is about to form in the middle.

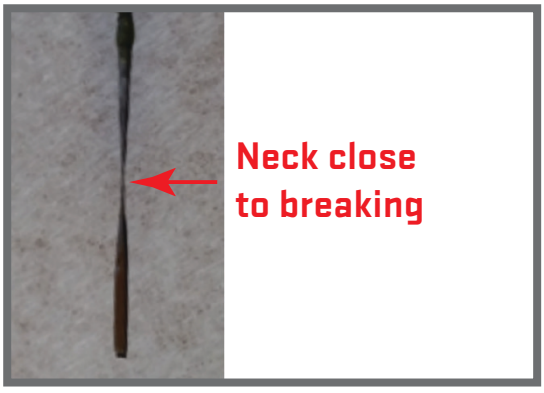



Fig. 9: A neck has been formed breaking one blank into two pieces of APT specimens.

# STEP-BY-STEP PROCEDURE

## 9 Breaking

**Method one:** Set the stop current to 1/3 of the measured current so the automatic polishing will be terminated when the neck breaks. Move to the next step, fine polishing. Usually the top portion that remains in the Cu stub is blunter, but the bottom portion is often ready for APT as-is.

**Method two:** This method controls the stop condition better, and thus makes the top portion sharper. To do so, fully immerse the neck into electrolyte. Move the electrode loop accordingly so it still moves in the necked region but always stays in the electrolyte solution. Reduce the voltage to lower the polishing rate. Apply short voltage pulses manually by quickly clicking on the voltage switch until the top and bottom portion separates. The top part in the Cu stub and the bottom part that falls into beaker produce two specimens.

Figure 10 is an example of the polishing that has ended automatically after the "neck" broke. The bottom portion has fallen into the beaker and the top portion is visible here.

If two sharp tips made from one blank (Figure 11), usually the bottom one that is retrieved from the beaker is sharper because milling stops immediately when the neck breaks.

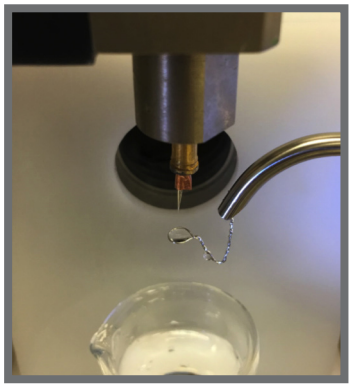


Fig. 10: The top half after electropolishing.

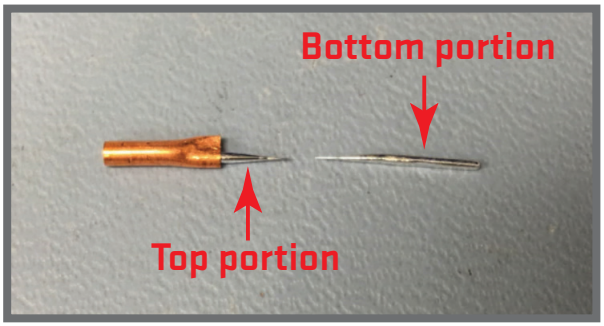



Fig. 11: Side by side comparison of the two parts.

## 10 Manual ElectroPointer (horizontal setup)

Figure 12 is an overview of the horizontal electropolishing set up which contains optical microscope w/ high magnification objective lenses, a variable voltage supply (DC and AC), a manual switch, a fixed stage for specimen holding, an electrolyte loop rig and sliding mechanism on the loop rig.

Some groups use only a vertical setup, some groups use only a horizontal setup, there are subtle advantages in different circumstances to either one. For the most versatile lab capability it is suggested to have both.

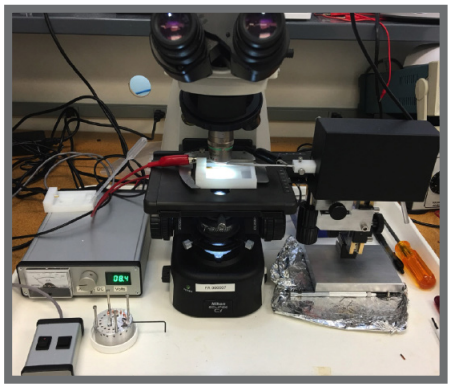


Fig. 12: Horizontal electropolishing set up for fine polishing.




Fig. 13: Voltage supply for DC and AC, and switch box for continuous mode and temporary/ intermittent mode.

# STEP-BY-STEP PROCEDURE

## 11 Loading for horizontal polish

Using tweezers to slide copper stub into the metal holder on the plastic block (Figure 14). It is a push and grab mechanism that can accept standard 1.8mm copper stubs.

Clamp the block in place on the X-Y mechanical stage (Figure 15). The electrolyte solution can be stored inside the depression on the plastic block for easy handling. Pipets rest on the holes that drilled in the plastic block when not in use.

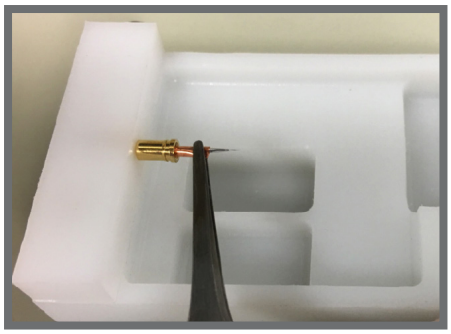


Fig. 14: Load crimped specimen in specimen holder.

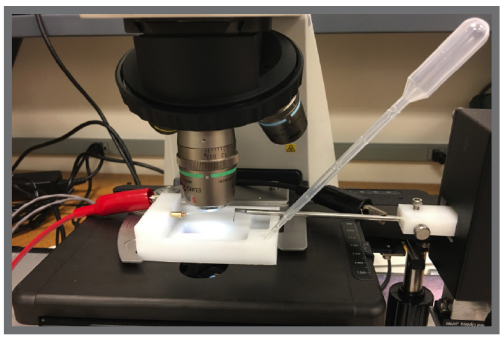


Fig. 15: Clamp stub into place using a tool.

## 12 Positioning

The specimen holder is placed on a optical microscope stage and is manually positioned so that the specimen moves into view through the microscope eyepiece.

The loop containing the electrolyte on a separate stage needs to be carefully aligned to the specimen so it move in and out in horizontal direction without shorting the circuit. The starting position should have both the specimen and the loop within the field of view from the eyepiece. Slide the loop in and out by pulling and releasing the lever on the loop stage. Choose continuous or temporary mode on the voltage switch box as needed. Temporary mode provides the most control over electropolishing speed.

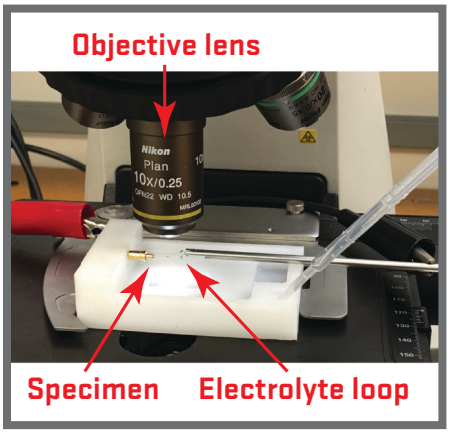



Fig. 16: Horizontal electropolishing configuration.

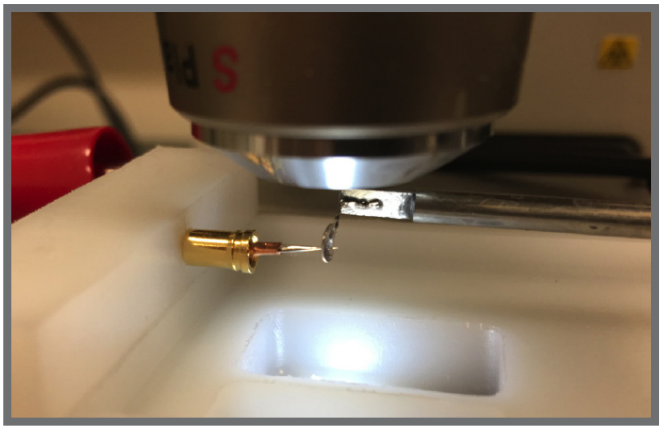


Fig. 17: Close-up view of specimen/loop configuration.

# STEP-BY-STEP PROCEDURE

## 13 Feeding electrolyte to the loop

Use a small jar to store the necessary amount of electrolyte for electropolishing. Use a larger beaker as a secondary container to avoid spilling as shown in Fig 18. Usually 1~2 ml is sufficient for re-sharpening specimens, 10ml or more if starting from wires/ matchsticks.

Use transfer pipet to transfer electrolyte to the loop. Refresh the electrolyte when it turns dirty. Using filter paper or a Kimwipe to 'wick off' consumed/dirty electrolyte on a regular basis is sometimes necessary depending upon the diameter of the sample or the specific alloy.

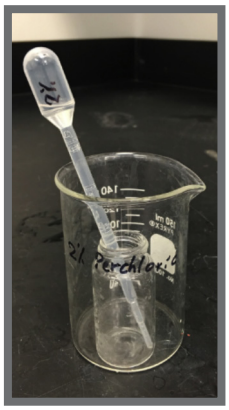


Fig. 18: Electrolyte stored in a jar with transfer pipet.

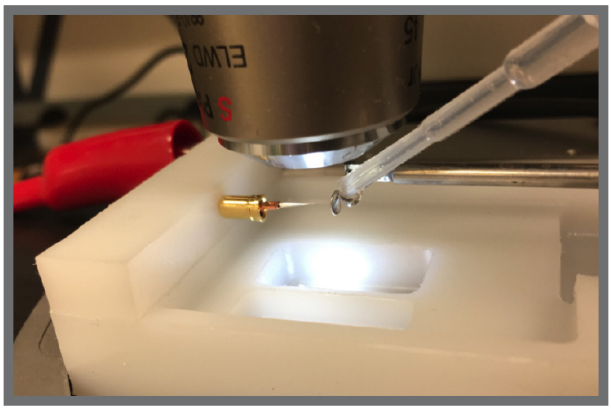


Fig. 19: Putting electrolyte on the loop.

## 14 Electropolishing procedure

To start the electropolishing process, a large drop of higher concentration acid can be used for rapid reaction.

When polishing at high reaction rates, the electrolyte will need to refreshed frequently.

Drag the electrolyte over the region where a neck is going to be formed while the desired voltage amplitude or type (AC or DC) is applied. Note that the polishing rate is always higher at the air-electrolyte interface.

As the neck keeps getting narrower, change to dilute electrolyte and reduce the voltage amplitude as needed.

To break the neck, use larger amount of electrolyte so the entire neck can be dipped into the electrolyte. Introduce voltage pluses manually and stop polishing once the neck breaks. **Note:** Typical starting voltages for steel are around 20-25 V DC



Fig. 20: Move electrolyte in and out to polish the desired region on the specimen.

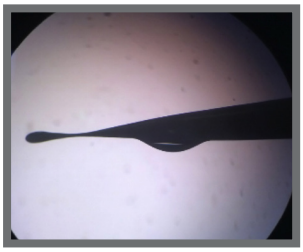


Fig. 21: A neck has been formed.



Fig. 22: The neck is about to break. Decrease the voltage and use a fresh drop of electrolyte in the loop to break the neck.

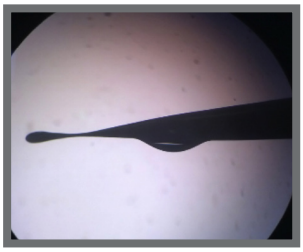


Fig. 23: Use manual switch control. Stop polishing immediately once the neck breaks is key to making sharp tips.

# STEP-BY-STEP PROCEDURE

## 15 Rinsing

Rinse the tip thoroughly by running chemical solvents (acetone, methanol, ethanol e.g.) down the tip from the copper stub. Use canned air or compressed, filtered, or dry nitrogen to blow the specimen dry. Dry the tip thoroughly before storing or analyzing.

Rinse the loop for storage before the next use.

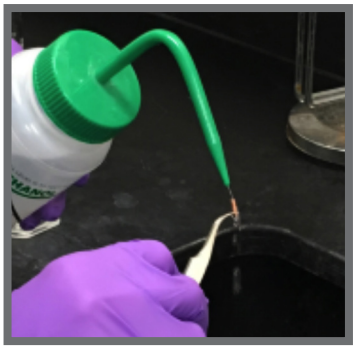


Fig. 24: Rinsing the specimen with methanol.

## 16 Final tip shape in SEM (if imaging is needed)

Take high resolution images of tip for shank angle and radius measurement if necessary. It is also possible to do tEBSD and EBSD/EDS analysis on ready to run tips.

The first few times doing electropolishing it is very useful to take notes for what your feeling of success on each tip was and to use an SEM to confirm optical inspection interpretation to SEM verifiable results

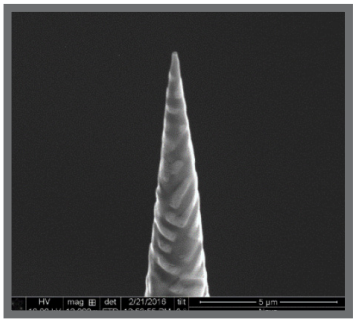


Fig. 25: Superalloy prepared by electropolishing. Imaging contrast reveals two phases in the material.

## 17 Recovering blade-shaped tips

If the prepared tip turns out to be in blade-shaped it can still be recovered by FIB. Even it involves FIBing the milling time can be significantly reduced by electropolishing.

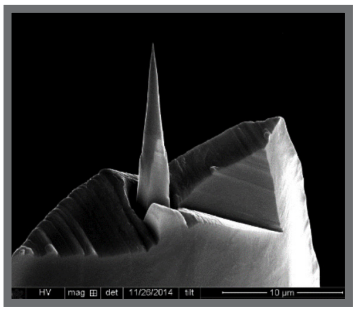


Fig. 26: Recovering blade tip using FIB.

## 18 Storage (sample block or cylinder)

Sample storage before or after APT analysis. Some electropolished samples oxidize very quickly and it is recommended that they be stored in a vacuum desiccator for long term storage if they are not going to be introduced into an atom probe right away.

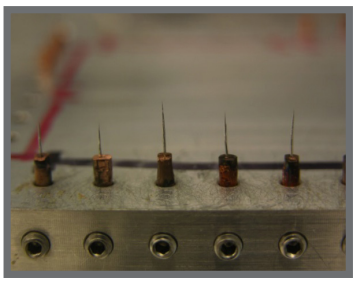


Fig. 27: Wires or roughly polished blank specimens stored in sample block or cylinder.

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APT Specimen preparation: Electropolishing
Document Number 30823
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