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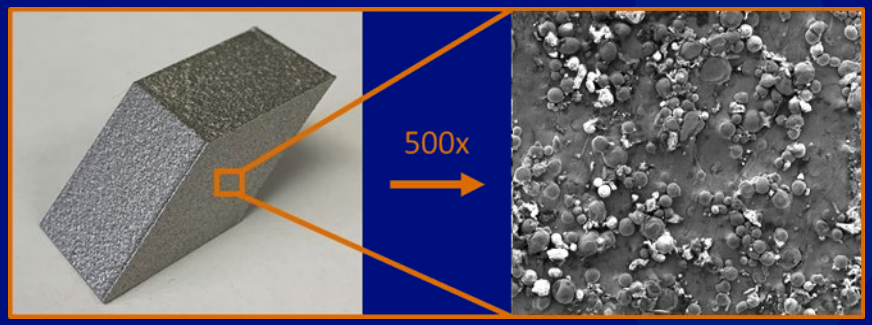
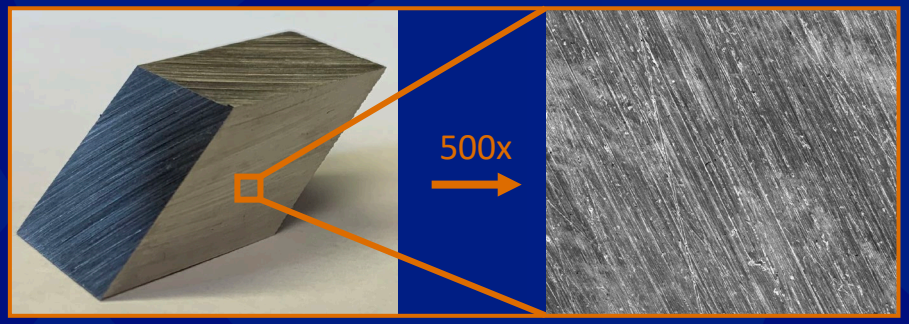
Pulse/Pulse Reverse Electropolishing of Additively Manufactured 316L Stainless Steel by NaCl/H_2O

Timothy Gorey, Daniel Hooks, Robert Hackenberg, Courtney Clark, Colt Montgomery, and Jamie Stull



Additive

S_a = ~10-12 μm



Machined

S_a = ~ 1 μm

Can AM materials have a similar finish to machining?

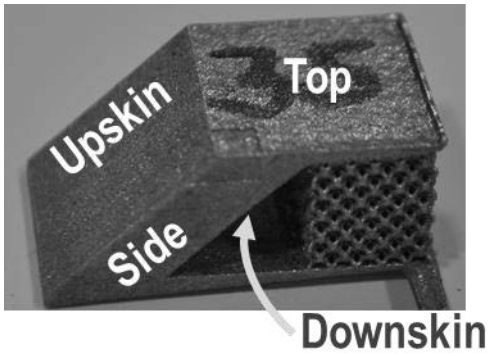
Metal Additive Manufacturing (MAM) is a powerful capability that can obtain high strength:weight components with complex geometry

Benefits MAM vs Traditional:

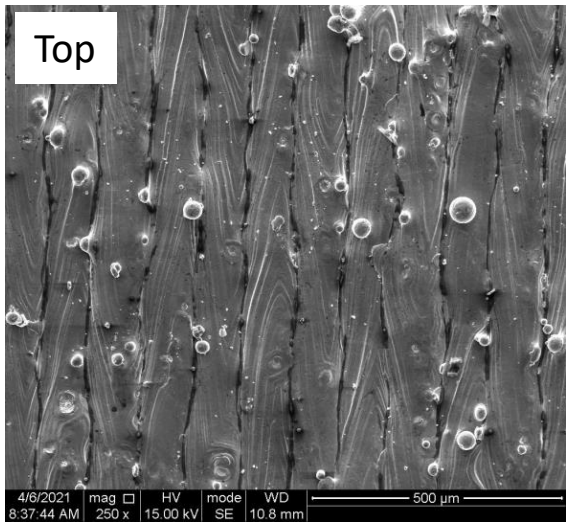
- Production is tightly connected to CAD design.
- High strength originating from complex geometries (e.g. lattices)

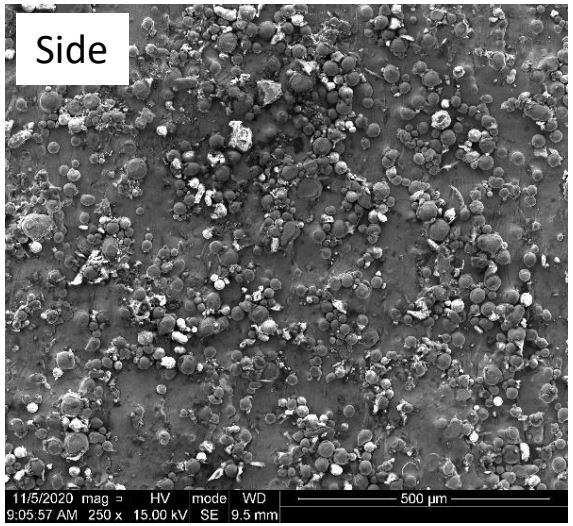
Limitations:

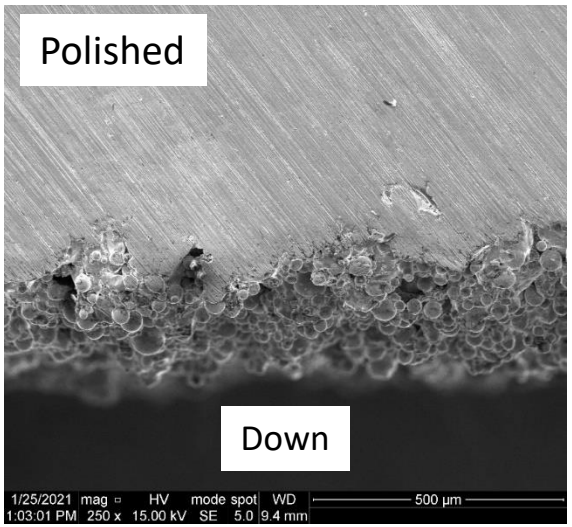
- Manufacturing is outpacing finishing capabilities
- As-built surfaces are rough, due to powder particle size
- Roughness-related issues: tolerance, corrosion
- Finishing solutions are needed for MAM part interchangeability



Microstructure varies with build orientation







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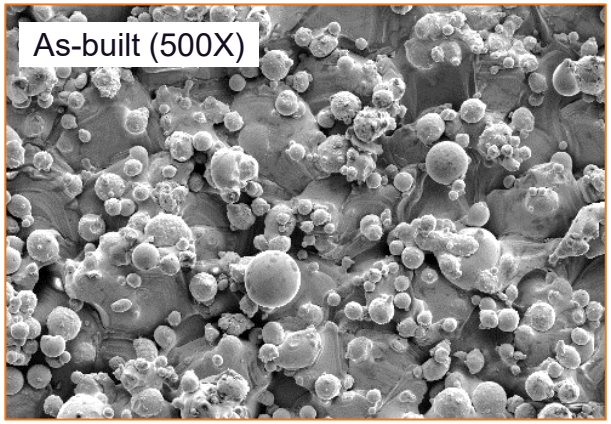
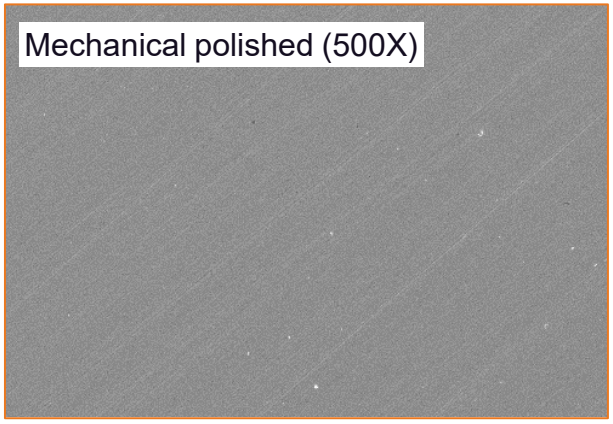
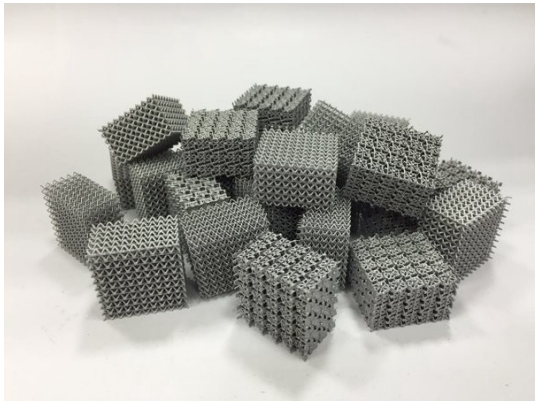
Images by Courtney Clark

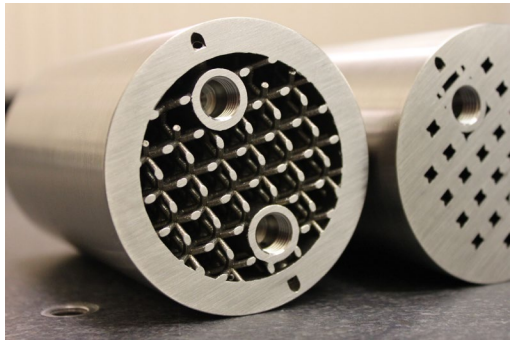
Dealing with Surface Roughness





Mechanical polishing is an effective finishing technique, but how do you apply it to components like this?





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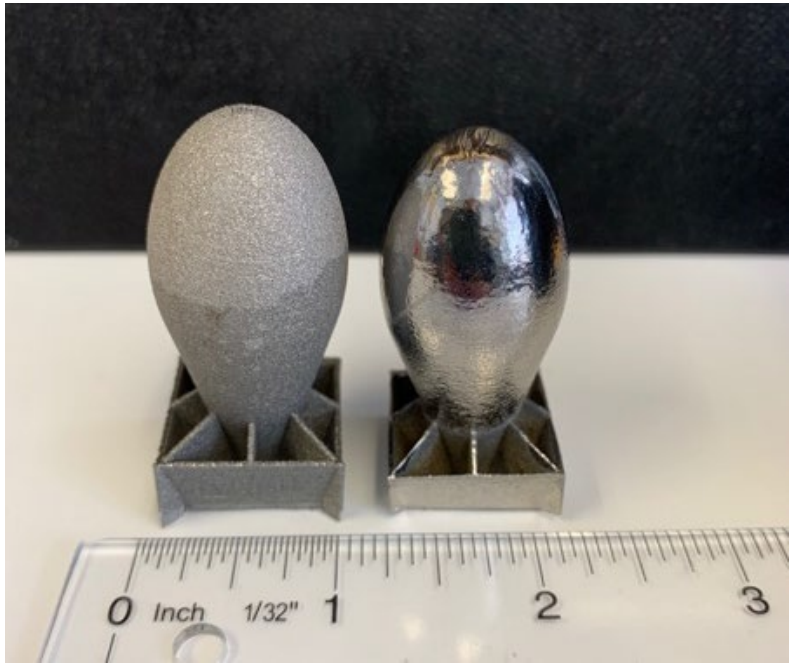
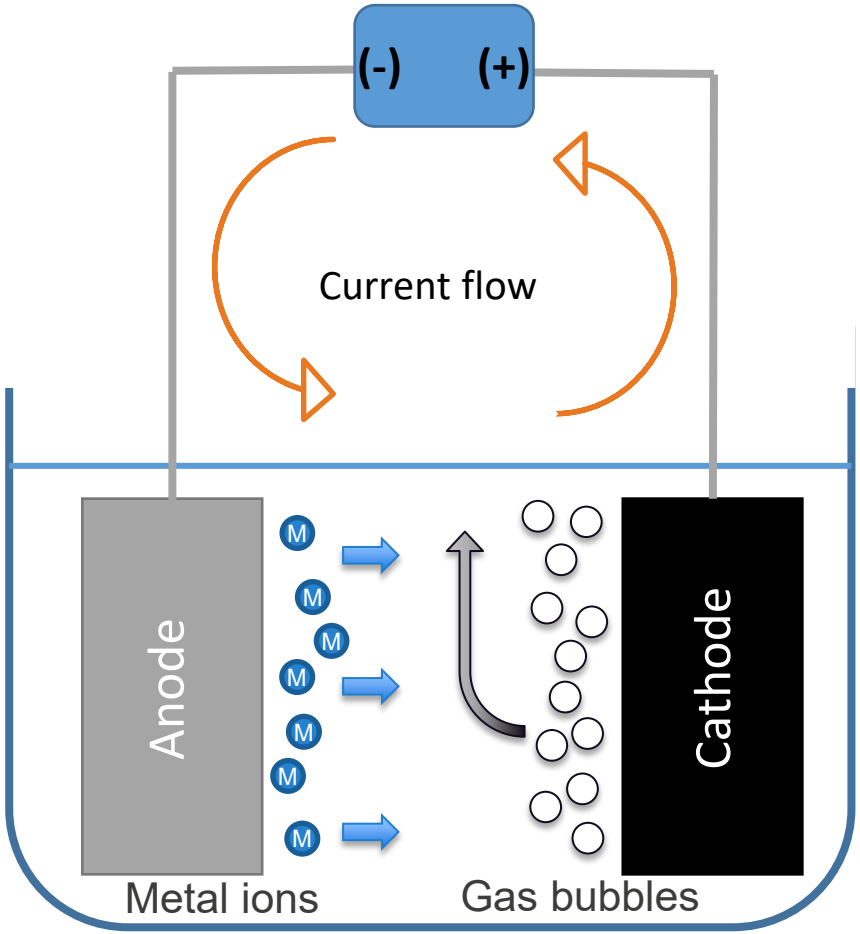
DC Electropolishing: H_3PO_4/H_2SO_4/Glycerol/HF

Electropolishing is a good solution for AM:
Full parts can be submerged, reaching internal surfaces

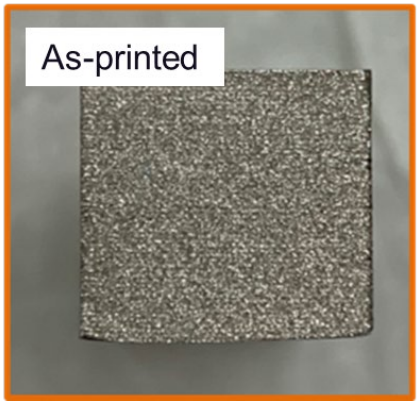


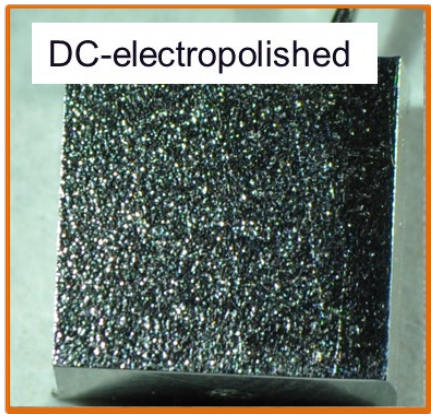


Anode: $M_{(s)} \underset{V}{\rightarrow} M^{n+} + ne^-$

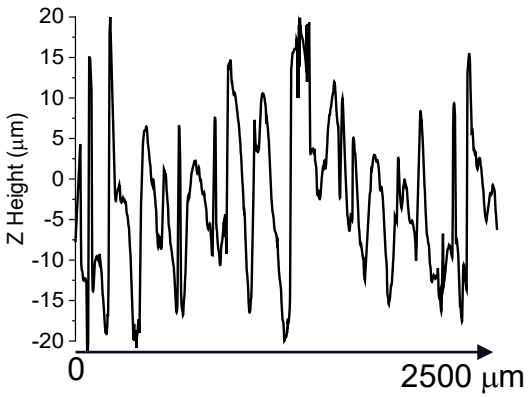
Cathode: $3H_2O_{(l)} + 3e^- \underset{V}{\rightarrow} \frac{3}{2}H_{2(g)} + 3(OH)^-$

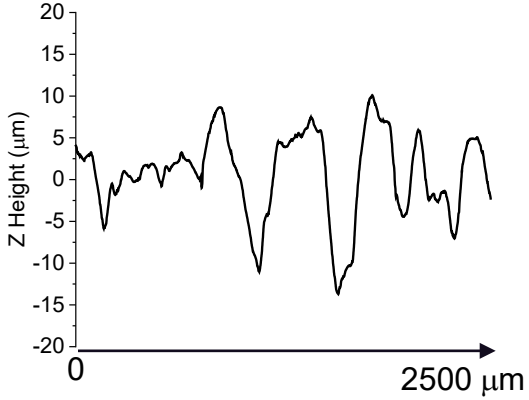
DC Electropolishing and Surface Roughness

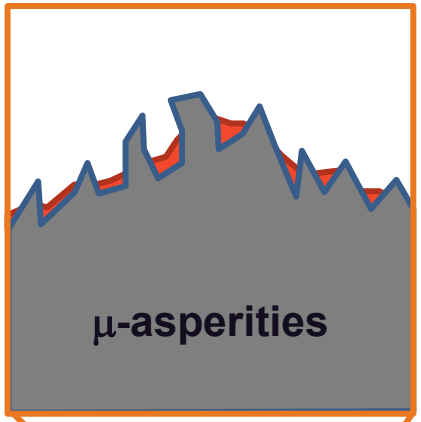


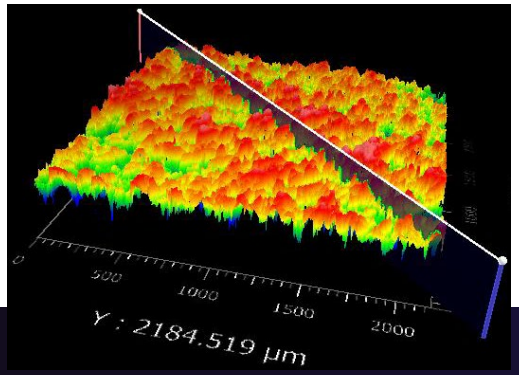


DC method gives a “mirror” finish but can’t smooth macro-asperities

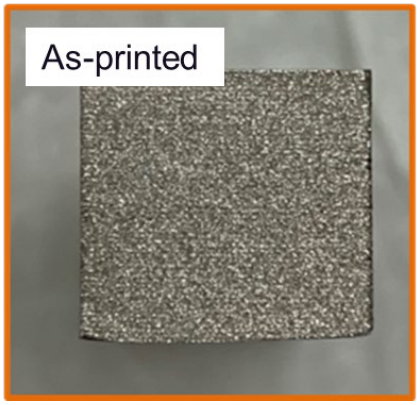


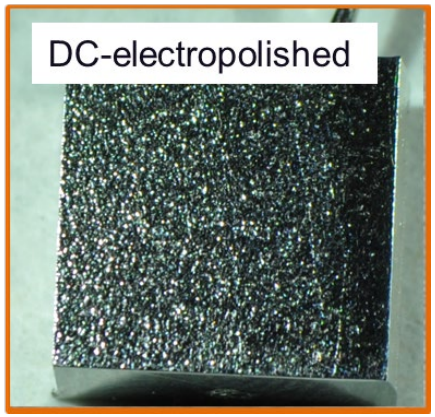






DC Electropolishing and Surface Roughness





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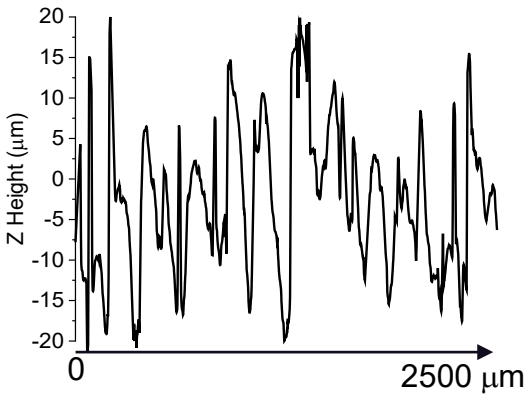
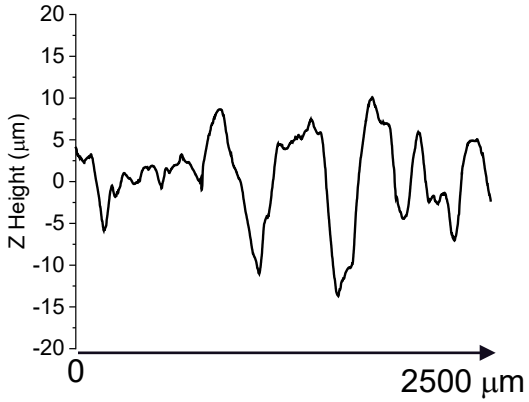
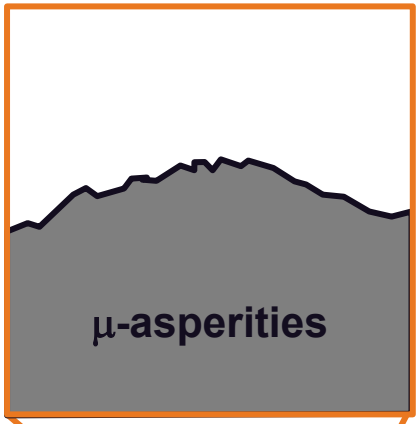
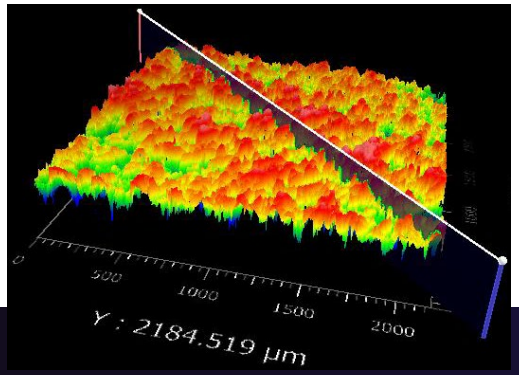








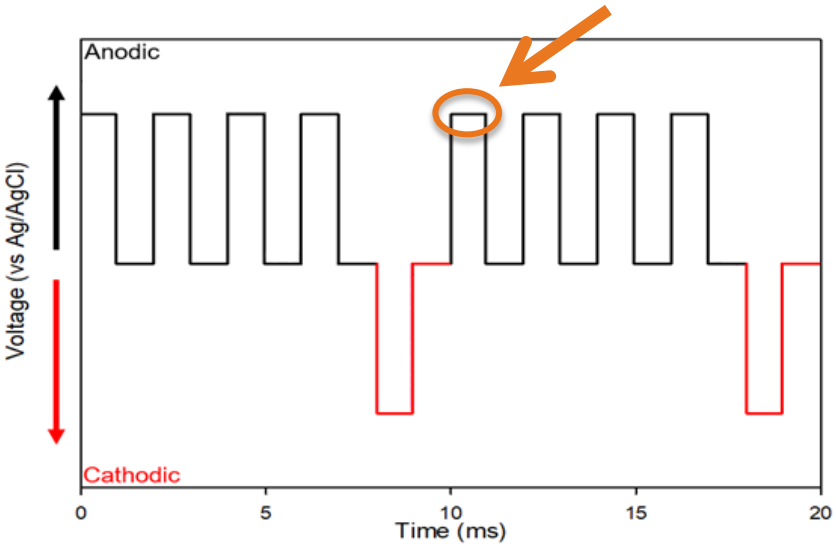
Pulse/Pulse Reverse Electropolishing

Hypothesis:

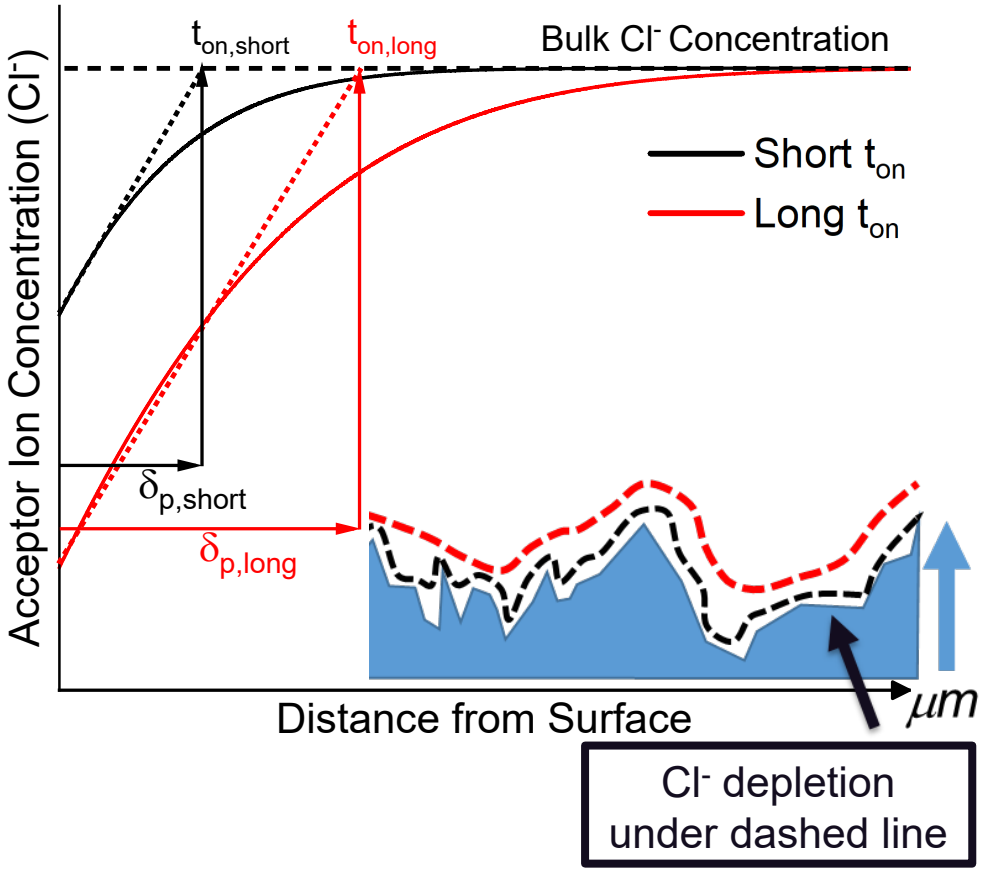
Use any electrolyte: $NaCl/Na_2SO_4$ in H_2O is compatible with dissolved metal

$$\delta_p \approx (2Dt_{on})^{\frac{1}{2}}$$

Depletion/ion layer thickness (δ_p) is controllable with t_{on}



Cathode pulses eliminate need for HF



Pure diffusion control: no concentrated acids

Pulse/Pulse Reverse Electropolishing:

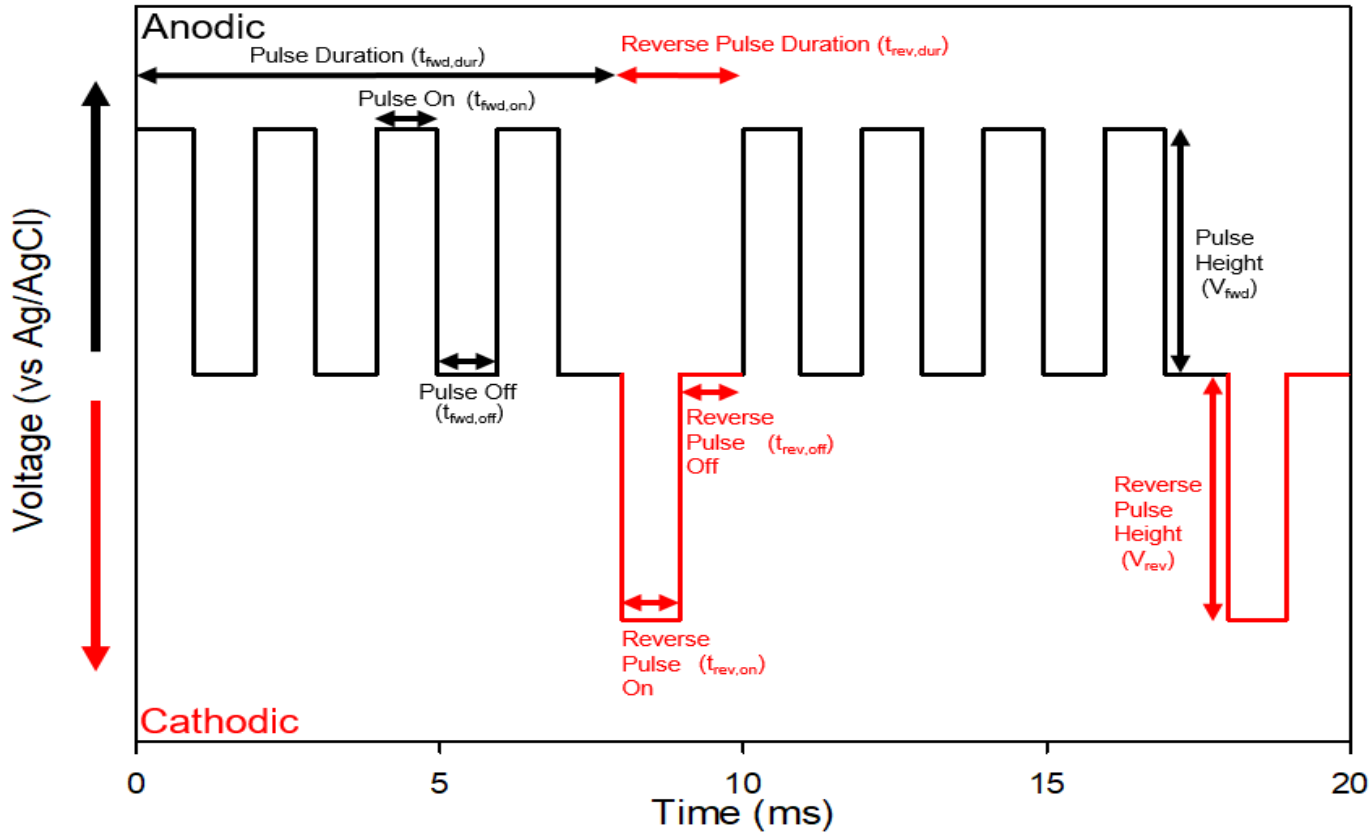
Summary:

Anodic pulses are sent to the work piece to etch asperities, and intermittent cathodic pulses are applied to depassivate the surface.

Challenge: high dimensionality

Solution conditions: chemical species, temperature, viscosity, resistivity

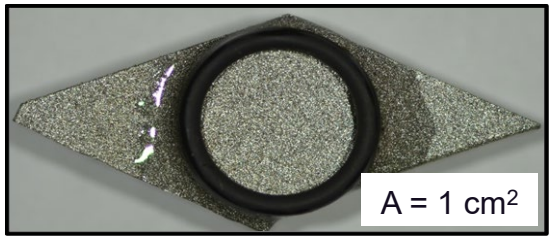
Potentiostatic: pulse on/off time, anodic/cathodic amplitude, duration, anode:cathode pulse ratio.

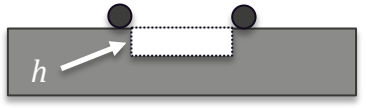


Pulse Parameter Experiments:

Goal:

Independently vary pulse/solution parameters and gauge surface finishing qualitatively (by inspection) and quantitatively (by profilometry).





$$V_{dissolved} = \frac{1\ cm^3}{7.8429g} \times \Delta M$$

$$h = \frac{V_{dissolved}}{1\ cm^2}$$

Controlled Experiments (key terms):

1.) **Effective Current**

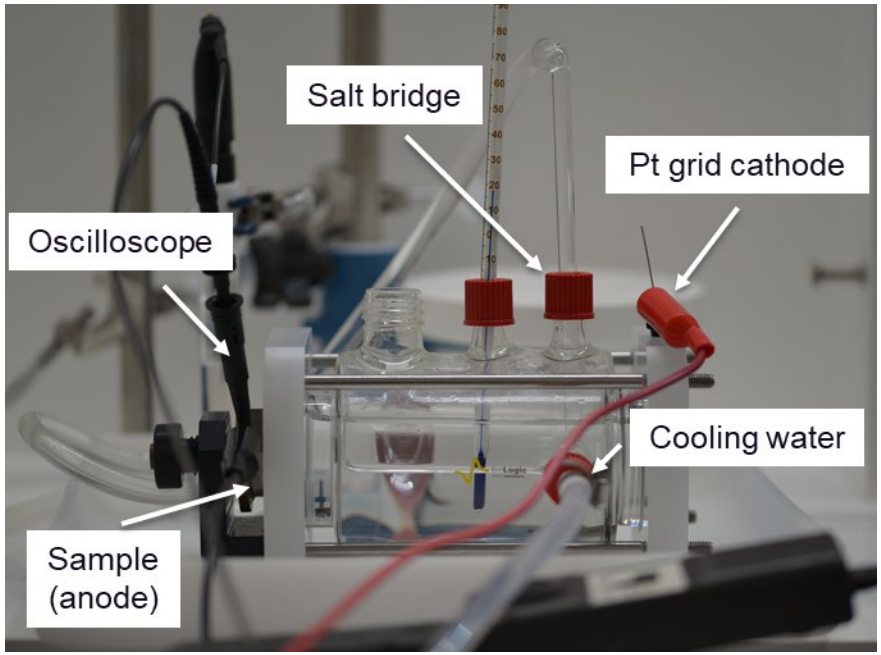
= Current the sample experiences, after accounting for on-times, off-times, and reverse pulses. (essentially an equivalent DC current)

$$Effective\ Current = \frac{Ampere}{cm^2}$$

2.) **Coulombic Density** (integrated current density)

= Total amount of charge transferred in the electropolishing process.

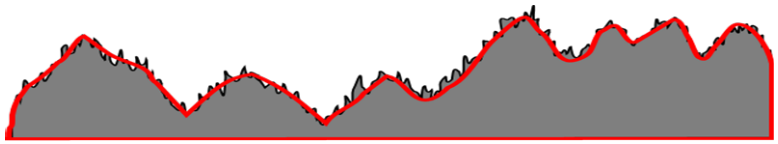
$$Coulombic\ Density = \frac{Ampere * min}{cm^2}$$



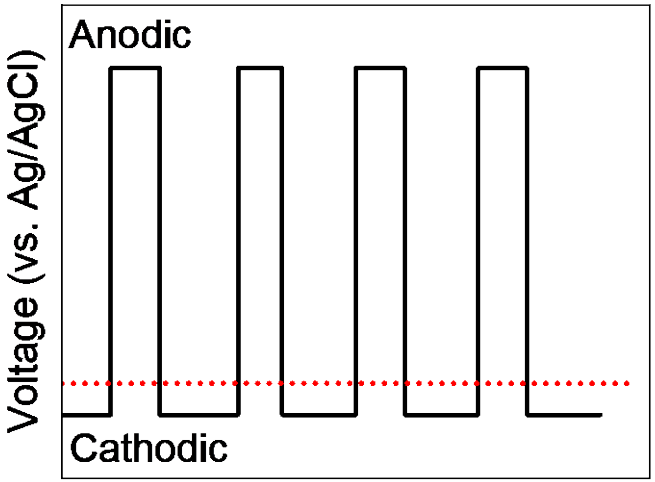
Choosing Pulse Parameters

(Figure adapted from that published by Faraday Technologies)

Targetting Macro-asperities

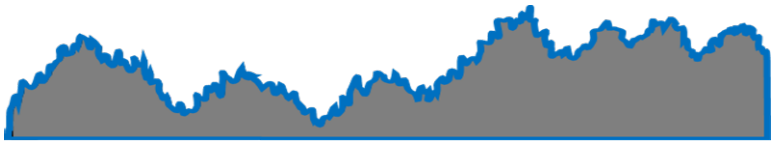


Short, intense t_{on} pulses generate a thin diffusion layer allowing for non-uniform smoothing, targeting macroasperities.

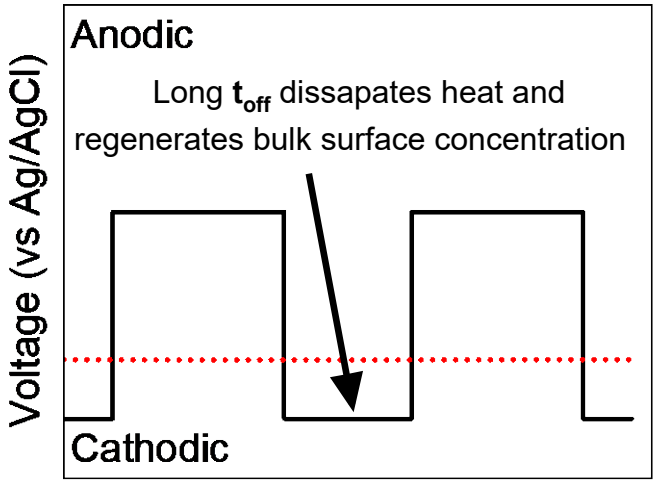


Macro-smoothed Surface

Targetting Micro-asperities

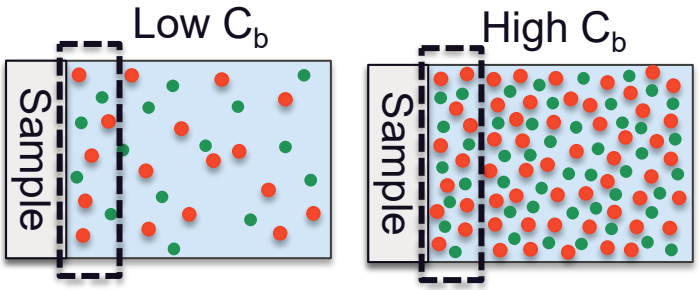


Long, t_{on} pulses generate a thick diffusion layer allowing for uniform smoothing, targeting microasperities. Lowering peak intensity lengthens transition time, maintaining a non-diffusion limited current distribution



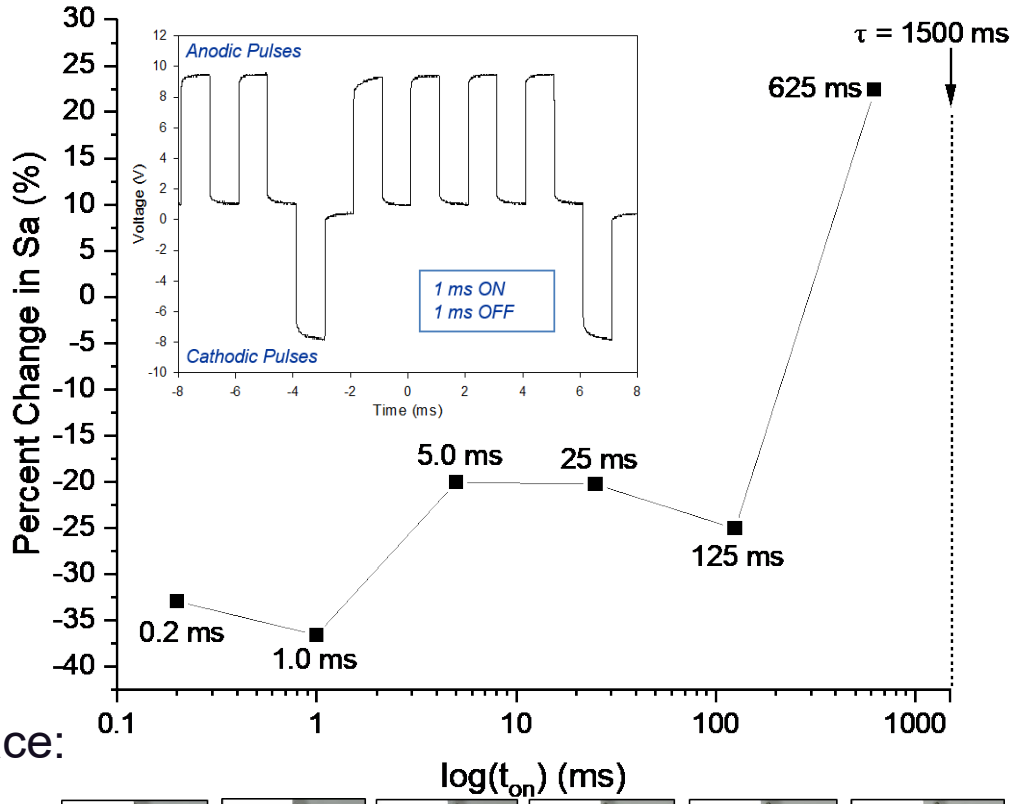
Micro-smoothed Surface

Choosing Pulse Width:



$$\tau = \frac{\pi\left((nF)^2 {C_b}^2 D\right)}{4{i_a}^2}$$

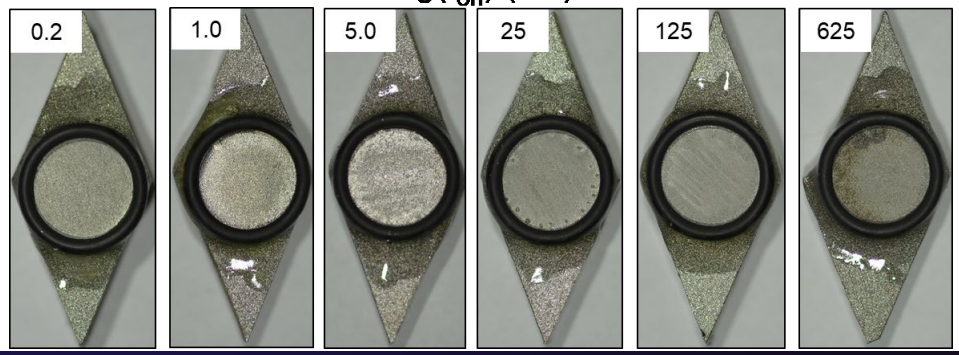
τ (transition time):
How long at a given current does it take to consume all reagents at the surface?



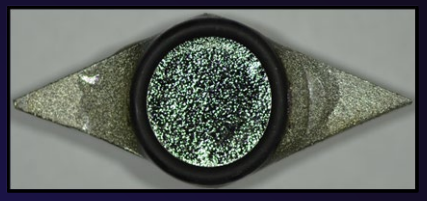
Factors outside mass transport alter surface:

1. Streaking at t_{on} > 1 ms (bubbles)
2. Pitting/corrosion at t_{on} > 5 ms
3. More severe corrosion at t_{on} > 125 ms

For the following experiments,
t_{on} = 1 ms will be used



Establishing a DC Basis for Comparison



DC Electropolishing Experiment:

- Roughness, mass, and SEM before/after electropolishing
- Follow polishing protocol established by electrolyte manufacturer. (E-Polish Solutions)

90 °C

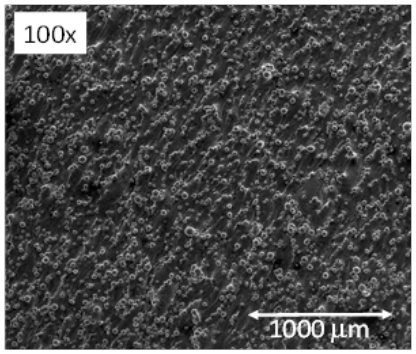
H_3PO_4/H_2SO_4

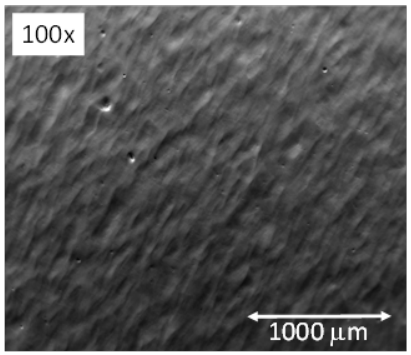
Current Density = 0.936 A/cm^2

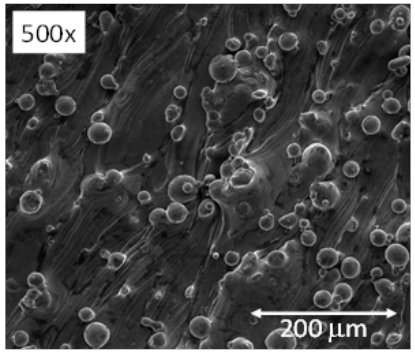
Coulombic Density = 15 A*min./cm^2

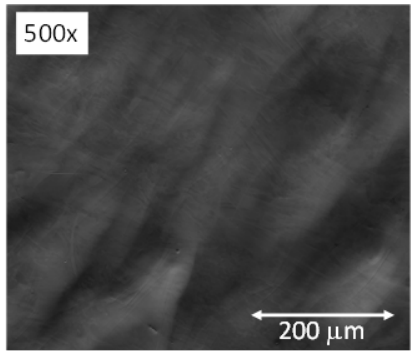
Results:

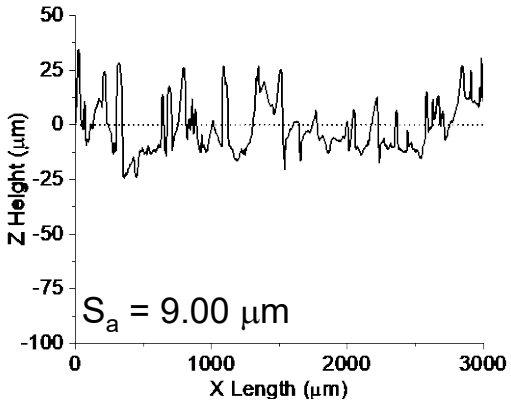
Micro-asperities are removed, mirror-like finish, 62 mg/ cm^2 material removed

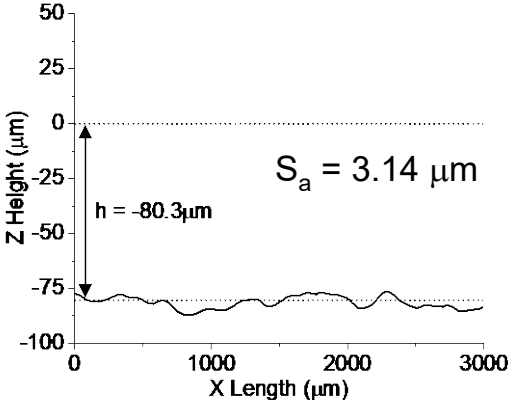












Pulse/Pulse Reverse Equivalent

P/PR Electropolishing Experiment:

- Define duration at same peak current and coulombic density.

$$I_{eff} = I_{anode,peak}(DC_{anode,eff}) - I_{cathode,peak}(DC_{cathode,eff})$$

$$DC_{eff} = \frac{Dur_{electrode} \cdot t_{on,electrode}}{(Dur_{anode} \cdot t_{on,anode}) + (Dur_{cathode} \cdot t_{on,cathode})}$$

- Determine change in mass/roughness

Conditions

2.5 °C

$Na_2SO_4/NaCl/H_2O$

Agitation: None

Peak Current Density = 0.936 A/cm^2

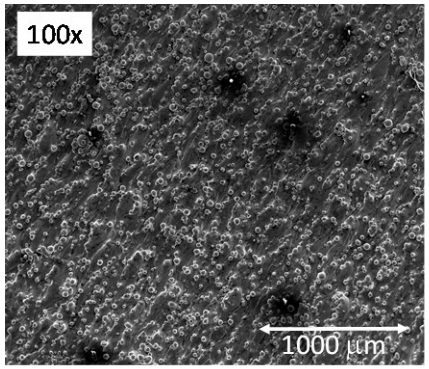
Coulombic Density = 7.5 A*min./cm^2

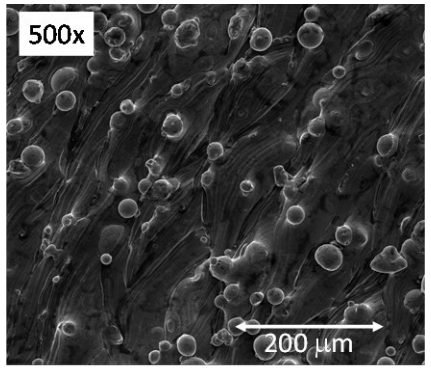
Results:

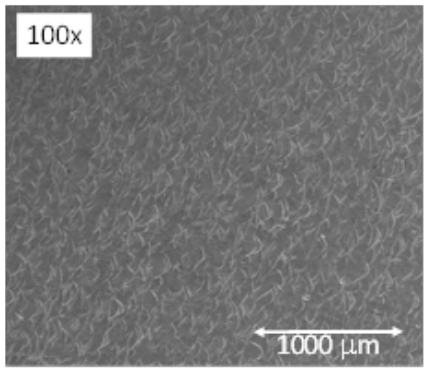
Considerably lower mass loss (12 mg/cm^2)

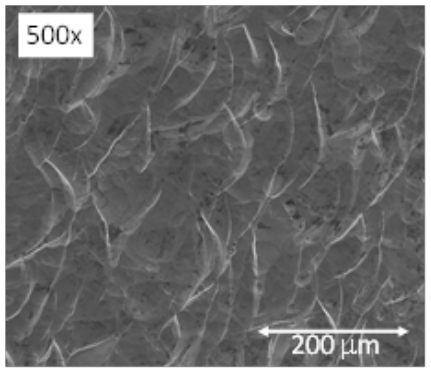
Surface roughness not as improved vs DC

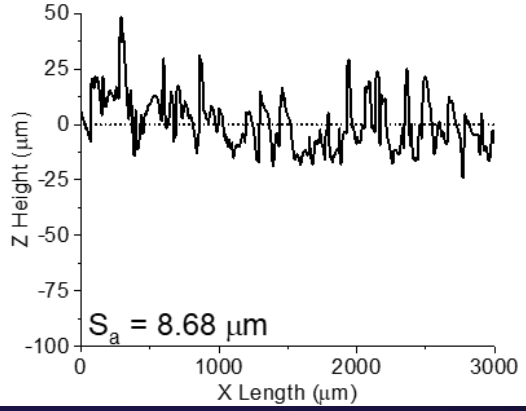
Fish scale-like microstructure

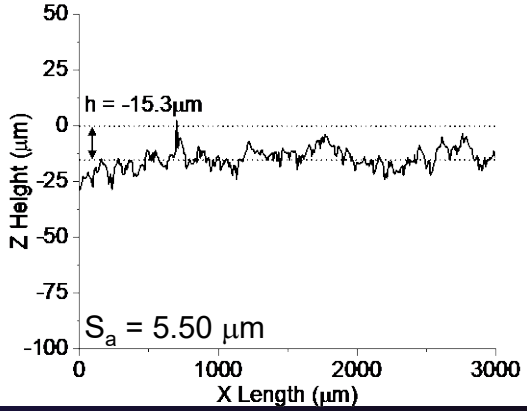




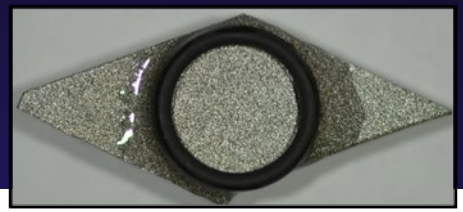


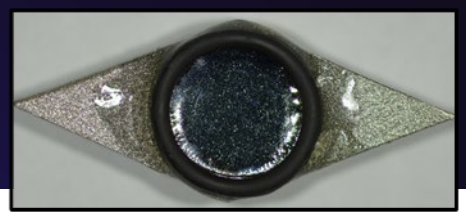






Two-Bath Electropolishing Method



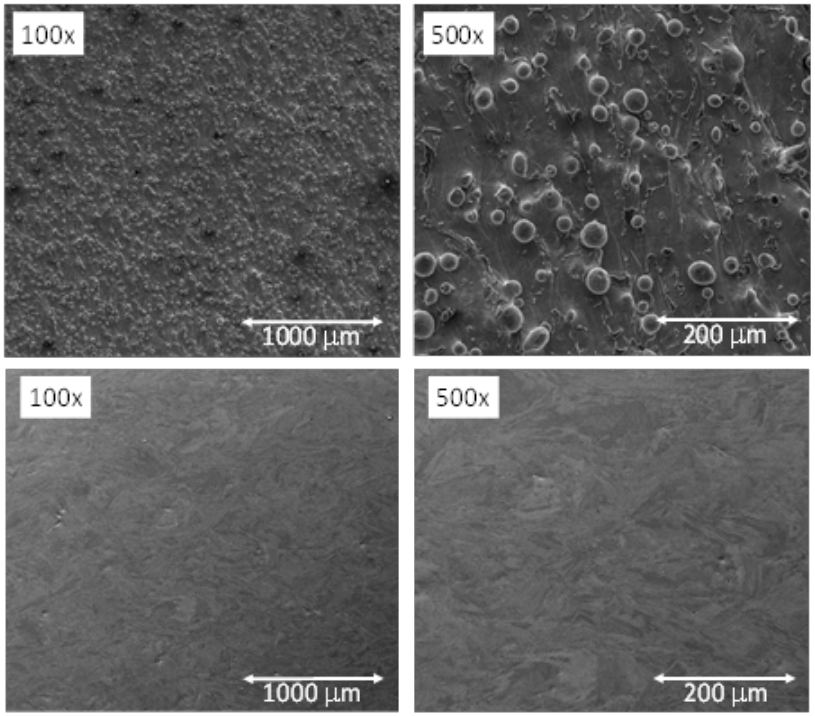


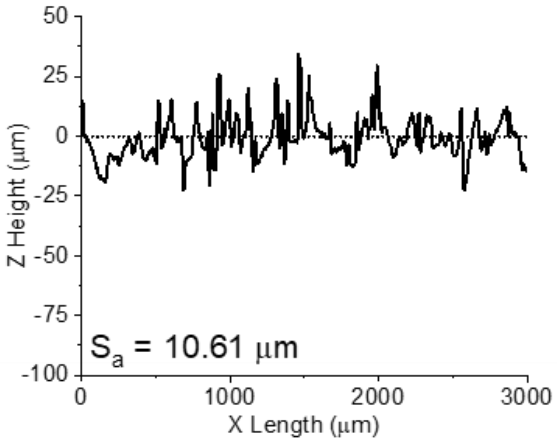
Procedure:

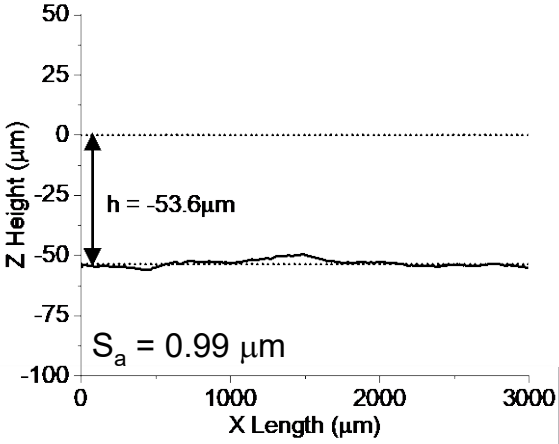
1. P/PR (NaCl) at 0.936 A/cm^2 up to 7.5 A*min/cm^2.
2. Determine $\Delta M/S_a$
3. DC at 0.936 A/cm^2 an additional 7.5 A*min/cm^2 (15 total)
4. Determine $\Delta M/S_a$

Results:

- Less mass loss(35 mg) compared to full DC method
- Most improved surface roughness
- Macro- and Micro-smoothing







Optimization of P/PR Sequence: Duration

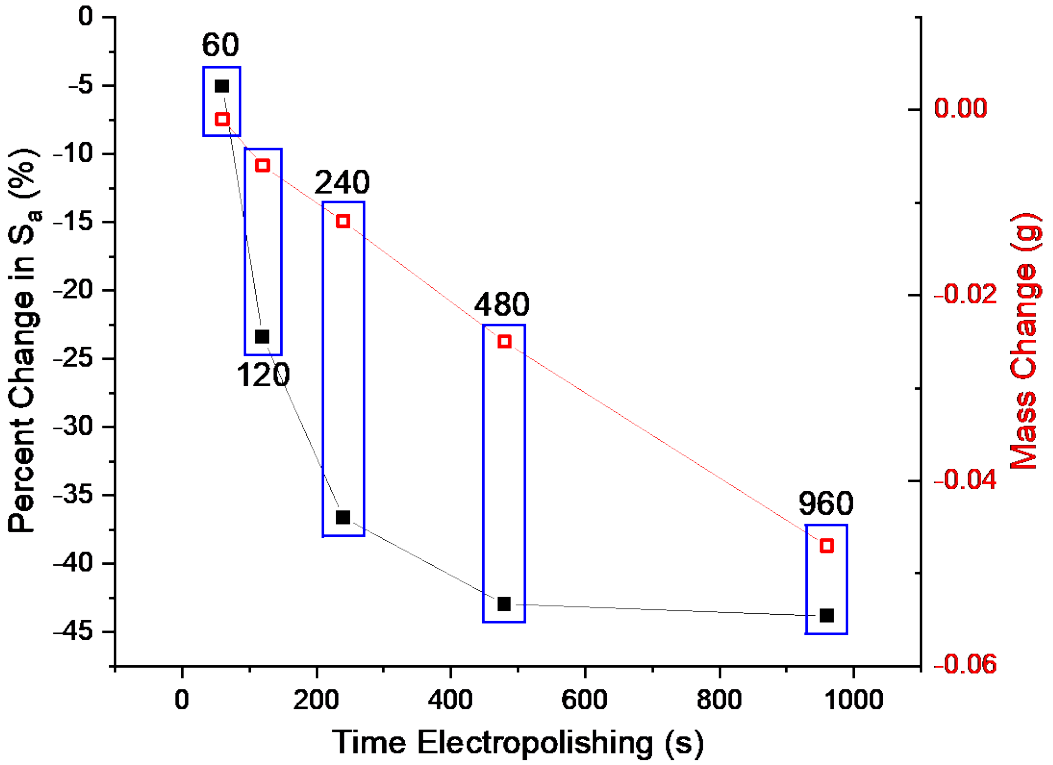
Varying Coulombic Density:

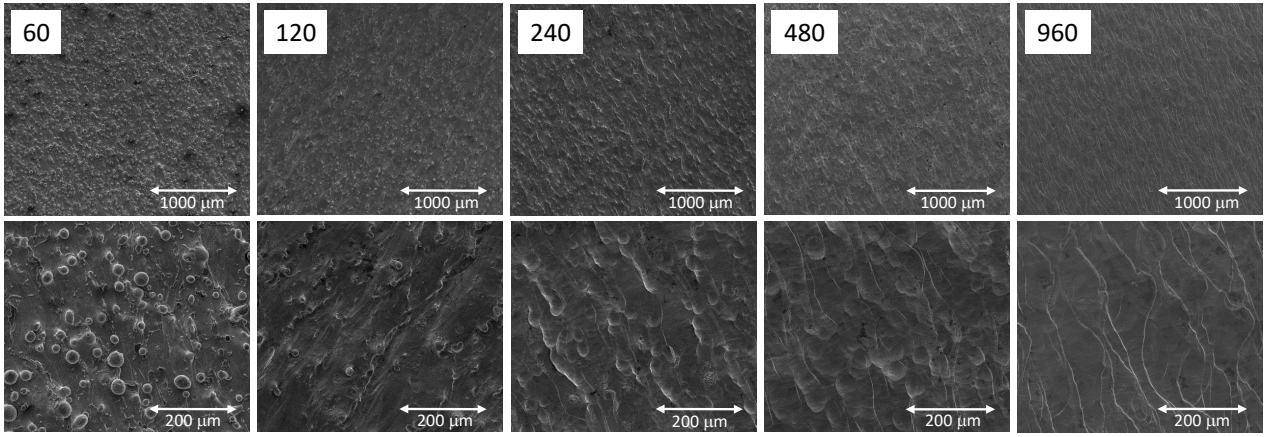
How does surface roughness change as the surface is increasingly etched?

Separate samples were electropolished at increasing durations: microstructure, ΔM, and $\%\Delta S_a$ are tracked.

Conclusions:

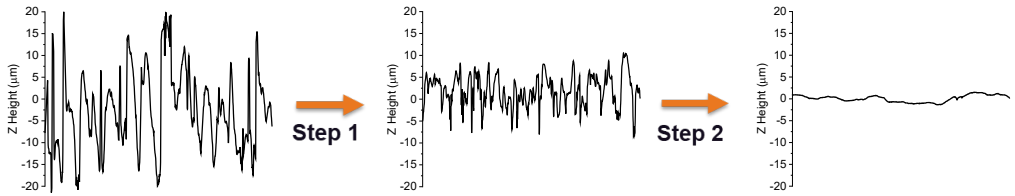
1. Mass decreases linearly with increasing coulombic density.
2. Surface roughness improves as a decaying function (diminishing returns)

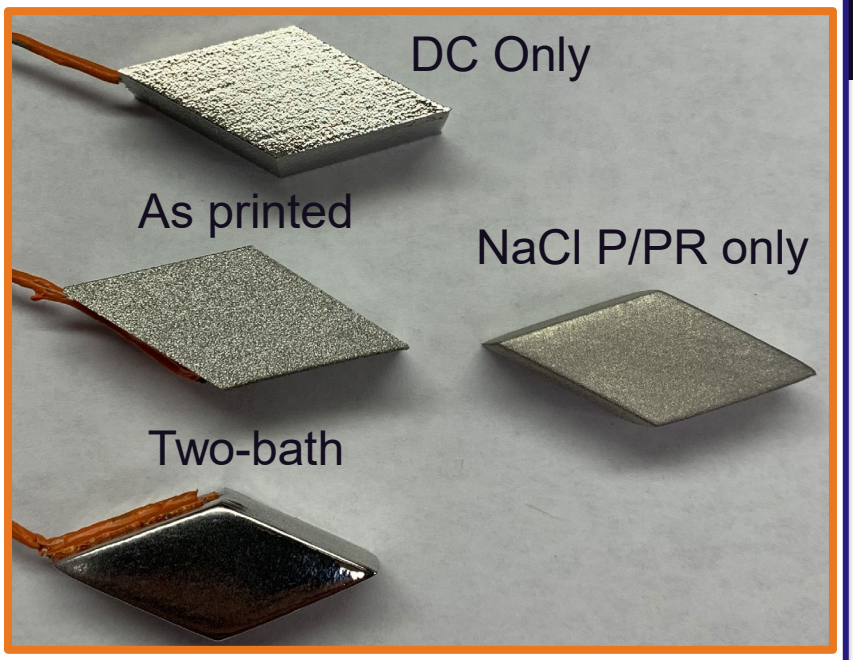




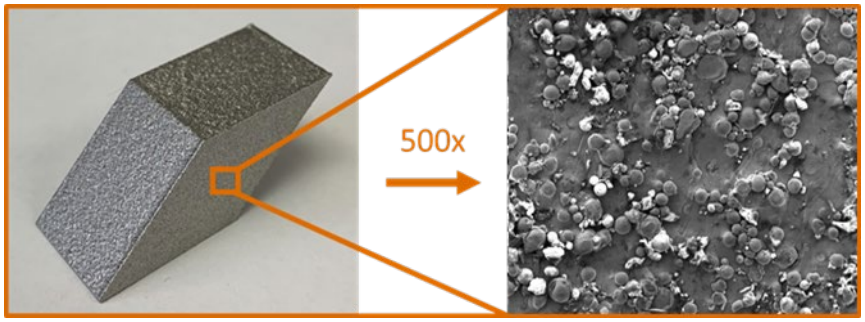
3D Components?

- Process can be scaled up with surface area
- Concerns with geometry changing
- Finite element modeling could be used to predict higher current density areas, use this to “over-print”



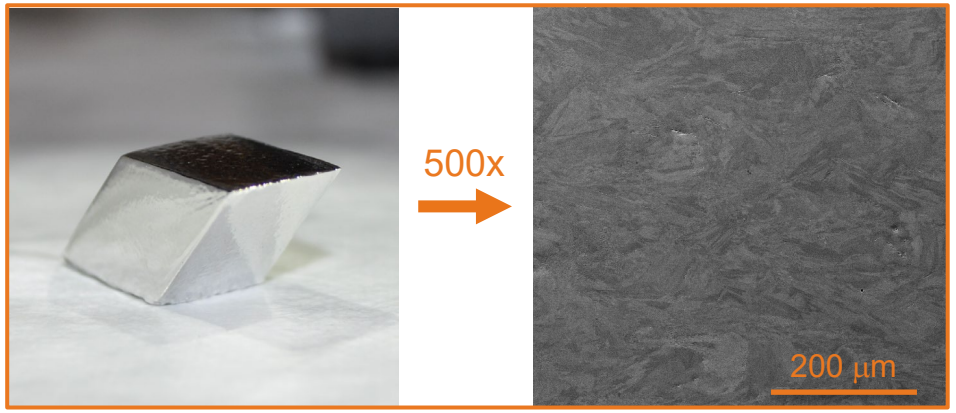


BEFORE



As-printed S_a = ~12 µm

AFTER



Additive: Two-bath S_a = 0.99 µm

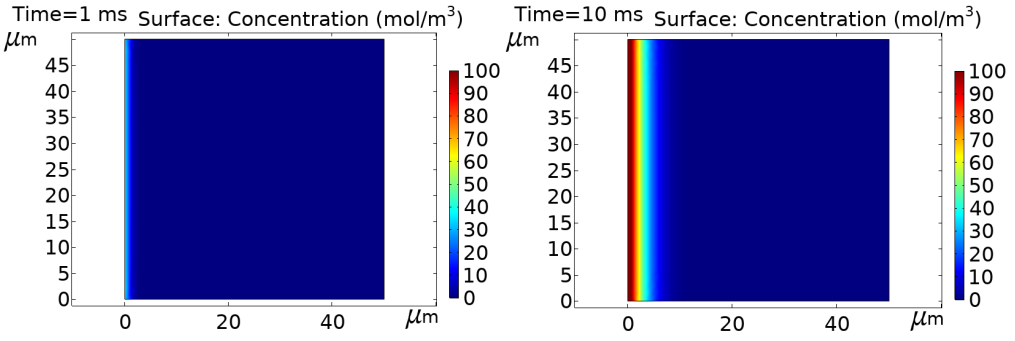
Rationalizing the Electrochemistry:

Physics to Consider:

- On-time: Nernst-Planck Equation:

$$J_i(x) = -D_i \frac{\partial C_i(x)}{\partial x} - \frac{z_i F}{RT} D_i C_i \frac{\partial \phi(x)}{\partial x} + C_i v$$

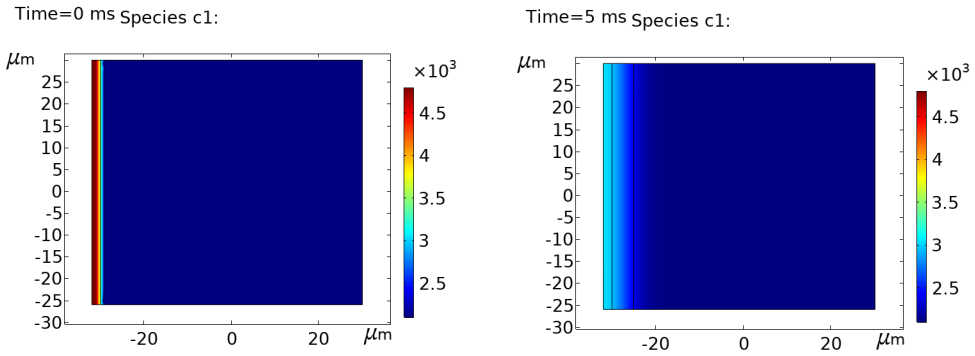
On-time also involves deforming geometry (i.e. dissolution) and current density distributions.



- Off-time: Fick's Law:

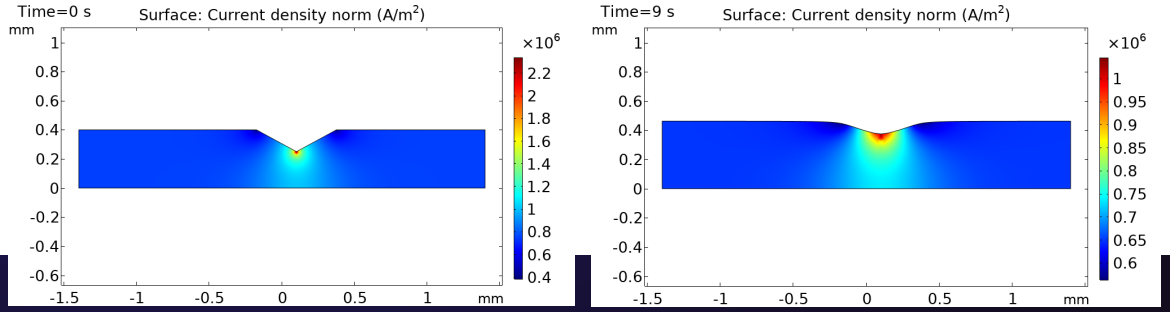
$$\frac{\partial C_i(x)}{\partial t} = D_i \frac{\partial^2 C_i(x)}{\partial x^2}$$

No electric fields or geometry changes



- Incorporating Geometry Change

Correlated with current distribution



Conclusions

DC Electropolishing:

- Limited to microsmoothing.
- Large mass loss/change in geometry.

Pulse/Pulse Reverse:

- Currently limited to macrosmoothing; unable to get mirror-like finish.
- Greatly reduced mass change for equivalent coulombic density.

Two-bath method:

- Currently able to macro- and micro-smooth full AM parts made of 316L Stainless steel.
- Less mass loss than traditional DC electropolishing, for equivalent coulombic density.

Future Work:

- Design pulse sequence to address micro-smoothing, i.e. single-bath method.
- Scale up to complex geometry (lattices)
- Extend technique to alternative materials (e.g. titanium, aluminum, etc).

Questions?