# Electrically Mediated Processes for Industrial Applications

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This technology is an electrochemical metal removal process that relies on state of the art electronics to apply a pulsed waveform to a conventional electrolytic cell. By applying the pulsed waveform, in place of a constant electric field, increased process control and enhanced surface finish can be realized in passive alloys, such as stainless steel and titanium alloys. The electrolyte used for this technology is environmentally safe, water-based, neutral salt electrolytes. Applications that may be presented are the surface finishing of titanium sputtering targets, hole drilling in stainless steel, and surface finishing of a nanocrystalline steel coating.

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## Introduction:

Many industries are currently experiencing the need for better product performance to succeed in today's global marketplace. Accompanying the need for enhanced performance is the need for cost reductions. To further complicate matters, advanced materials that were tailored for high end applications are now being seen in more mainstream applications. Advanced finishing methods are being used more and more to provide the enhanced surface characteristics required.

State of the art in advanced finishing methods includes: thermal energy methods (TEM), electropolishing, and abrasive flow finishing. Although these processes can produce excellent results in specific applications, limitations may exist for expanding into new applications. For example, TEM has limitations involving maximum burr size and may invoke material property changes due to heat build up in some alloys.[1] Furthermore, TEM would not be an appropriate selection for a surface finishing application. Electropolishing, which is a standard process in both the semiconductor and medical device industries, utilizes concentrated acids that result in relatively low removal rates and pose a significant threat to both worker and environmental safety. Electropolishing would not be suitable for applications looking for heavy burr removal.

This paper identifies a novel edge and surface finishing technique that was developed to address a wide range of engineering materials (from plain carbon steel to cast aluminum to advanced, high temperature alloys used in the aerospace industry) yet provide the flexibility to adapt to a variety of applications, including both edge deburring and surface finishing. This process is based on the same fundamental principles that govern electrochemical machining (ECM). ECM boasts a significant number of advances over conventional machining methods, such as milling and turning, including the ability to: (1) achieve high removal rates, (2) machine extremely hard materials without loss of high machining rates and (3) machine complex, burr free surfaces. Furthermore, the ECM process is non-contact, resulting in a process that does not induce residual stresses or realize tool wear. The advanced technique addressed in this paper enhances the ECM process through the use of a pulsed electric field (i.e. electrical mediation). Through the utilization of these pulsed waveforms, the novel technique realizes an increase in process control, which can ultimately provide a better final product (e.g. enhanced surface finish). Finally, the electrically mediated process shifts the need from aggressive chemical baths to allowing the use of water based, neutral salt solutions. This alleviates the worker and environmental safety concern associated with chemically mediated processes.

## Introduction to Electrically Mediated Process Parameters

At the heart of electrically mediated processes is the pulsed electric field. The electric field is obtained via a computer controlled power supply with the asymmetric waveform shape being entirely user defined. The shape of the waveform distinguishes this process from conventional, direct current (DC) electrochemical processes where the only user defined variable in terms of the electric field is a constant current or voltage value. This section identifies the parameters of the waveform that are available to the user.

A typical waveform consists of a forward pulse held for some duration of time ($V_{for}$ and $t_{for}$) followed by an off period ($t_{off}$) where no current is passed. For enhanced process control, a reverse pulse held for a set period of time ($V_{rev}$ and $t_{rev}$) may be necessary. The period of the waveform is the summation of the on times and off time. The frequency is the inverse of the period. The duty cycle is defined as the ratio of the on time to the period. Duty cycles are defined for both the forward, $\gamma_{for}$, and reverse, $\gamma_{rev}$, pulses. The average voltage, $V_{ave}$, is defined as:

$$V_{ave} = V_a \gamma_a - V_c \gamma_c \qquad \text{(Eq 1)}$$

where,

$$\gamma_a + \gamma_c \leq 1 \qquad \text{(Eq 2)}$$

The average voltage influences the material removal rate, the dimensional accuracy, and the surface quality. Simple examples of pulsed waveforms are shown in Figure 1.

For a given average voltage, traditional DC processes are limited to only one process

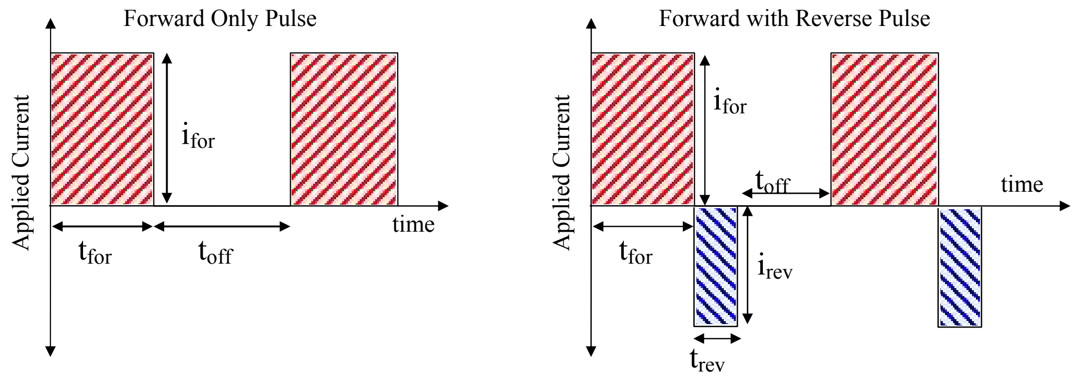


Figure 1: Simple Examples of Pulsed Waveforms

variable (the steady-state voltage or current). In an electrically mediated process, however, there are nearly an infinite number of process parameter combinations that can provide the desired average voltage. By selecting the appropriate combination of parameters, the mass transport rate, current distribution, and hydrodynamic condition can be strongly influenced during the metal dissolution process. A brief discussion regarding these conditions is given in the following paragraphs.

*Mass Transport*

In electrically mediated processes, mass transport is a combination of steady state and non-steady state diffusion processes. The theory of mass transport during non-steady state electrolysis has been previously discussed.[2,3,4] In DC processes, the diffusion layer thickness, $\delta$, is time invariant and is defined by the electrode geometry and solution hydrodynamics. In electrically mediated processes, $\delta$ varies from 0 at the beginning of the pulse to its steady state value when the Nernst diffusion layer is fully established. Since the diffusion limiting current density is inversely proportional to the diffusion layer thickness, this analysis would suggest that $\delta$ is infinite at $t = 0$ and would eventually decrease to a steady state value equivalent to the DC limiting current density. If the pulse duration is kept small, however, $\delta$ cannot achieve its steady-state value. During the subsequent off period, the reacting ions diffuse back to the electrode surface, replenishing the surface concentration to its original value. Therefore, the concentration of the reacting species, in the vicinity of the electrode, pulsates with the applied waveform. By selecting the appropriate duty cycles, the concentration profile of the reacting species at the beginning of each pulse can be kept relatively constant.

Theoretically, a "duplex diffusion layer" consisting of a pulsating layer, $\delta_p$, and a stationary layer, $\delta_s$, has been proposed for electrically mediated processes.[5] By assuming a linear concentration gradient across the pulsating diffusion layer and conducting a mass balance, the pulsating diffusion layer thickness ($\delta_p$) was derived:

$$\delta_p = \sqrt{CDt_{for}} \qquad \text{(Eq 3)}$$

where $C$ is a constant and $D$ is the diffusion coefficient. The limiting current density, $i_{pl}$, in electrically mediated electrolysis, is:

$$i_{pl} = nFD(C_s - C_b)/\eta_p\delta_p \qquad \text{(Eq 4)}$$

The limiting current density in the steady state condition is:

$$i_l = nFD(C_s - C_b)/\eta\delta \qquad \text{(Eq 5)}$$

Therefore, the relationship between the limiting current in the steady state condition and the non-steady state condition is:

$$\frac{i_l}{i_{pl}} = \frac{\delta_p}{\delta}\left(1 - \gamma_{for}\right) + \gamma_{for} \qquad \text{(Eq 6)}$$

Since $\delta_p \ll \delta$ and $\gamma_{for} < 1$, a higher limiting current density can be applied in an electrically mediated process, as compared to steady state conditions (DC). This increase in limiting current density directly relates to higher, instantaneous removal rates.

*Current Distribution*

The current distribution directly influences the material removal rate, the dimensional accuracy, and achievable surface finish. In DC processes, the current distribution is controlled exclusively by primary, or geometrical, effects. Through the addition of a pulsed electric field, the current distribution in an electrically mediated process is controlled not only by primary effects but also by secondary (kinetic) and tertiary (mass transport) effects. Compared to primary current distribution alone, the addition of kinetic or tertiary effects tends to make the current distribution more uniform. The extent of the influence of both the kinetic and mass transport effects is controlled by proper selection of waveform parameters. Therefore, the applied waveform can generate either a localized current distribution for edge finishing applications or a uniform current distribution for surface finishing applications.

*Hydrodynamic Conditions*

As in all electrochemical applications, non-uniform hydrodynamic conditions within the interelectrode gap can adversely affect the results of an otherwise ideal process. In the case of an electrically mediated process, control of the hydrodynamic condition is critical to fully realize the enhanced control mechanisms discussed in the previous two sections. To promote uniform hydrodynamic conditions in the gap between the tool and work piece, an electrically mediated waveform includes an off and/or reverse period. It is during these periods that the waste products (in the form of heat, gas, and metal precipitates) are flushed from the machining gap. Unlike conventional DC processes that cannot benefit from such a break in the forward pulse, the electrically mediated process can effectively flush the gap with relatively low flow rates, minimizing cavitation issues that often plague high flow rate processes. Furthermore, the nascent hydrogen gas generated at the tool during the forward pulse can be anodically consumed during the reverse period. By consuming the nascent hydrogen in the interelectrode gap, the electrolyte density, thermal conductivity, and flow velocity is more uniform. A detailed discussion on the effects that hydrodynamic non-uniformity has on ECM processes has been provided by Kozak et al.[6]

*Conclusions*

Compared to state of the art finishing techniques, electrically mediated processing provides a non-contact means of achieving extremely smooth surfaces with relatively high removal rates, even on hard, passive alloys. This process utilizes simple, water based electrolytes that are worker and environmentally safe.

Compared to DC electrochemical processes, the electrically mediated finishing process can: (1) provide enhanced control of the current distribution, (2) achieve uniform electrolyte properties within the interelectrode gap by removing waste products during the reverse and off times, (3) achieve a high limiting current density resulting in a relatively high removal rate, (4) reduce the necessary electrolyte flow rate thereby minimizing cavitation concerns, and (5) minimize oxide film formation on the part surface, allowing the polishing of passive alloys.

 

**Prior Work**

In previously reported work, Faraday Technology, Inc. has shown capability in the following areas. Some of these milestones may be presented at the conference:

- Electrically mediated edge finishing of cast aluminum alloy wheels [7, 8]
- Electrically mediated edge and surface finishing of stainless steel valves [8]
- Electrically mediated surface finishing of titanium and titanium alloys [8, 9]
- Engineering study to determine tool life for electrically mediated surface finishing of 316 stainless steel[10]
- Electrically mediated edge finishing of titanium medical clips[10]
- Electrically mediated edge finishing of surgical steel blades[10]

**Industrial Examples**

The following examples are ongoing work at Faraday Technology, Inc. A brief description of each example is provided. These examples may be presented at the conference:

- Surface finishing of titanium sputtering targets,
- Surface finishing of a commercially available, nanocrystalline steel coating,
- Non-Contact/Zero-Stress Polishing Process for Cu/low-*k* Semiconductor Applications, and
- Electrically mediated hole drilling.

*Surface Finishing of Titanium Sputtering Targets*

In this commercially funded project, the objective is to remove a small amount of material from the surface of a pure titanium sputtering target. A process was developed by Faraday to provide a 0.4µm (16µin) Ra surface finish on representative coupons. The electrolyte used was a simple, water based electrolyte. Bench scale feasibility was proven using a parallel flow cell fixture. The design of this versatile apparatus allows one to quickly develop the necessary parameters to achieve the best process.

Upon successfully achieving feasibility, design efforts were underway to transition the developed process from coupons to an actual full size target (approximately Ø300 mm). The final design of the apparatus calls for relative motion between the tool and target. The intent of the motion is to minimize power consumption and the width of the tool (measured perpendicular to the flow) to aid in maintaining uniform electrolyte properties. Photographs of the apparatus and control panel are shown in Figure 2.

 

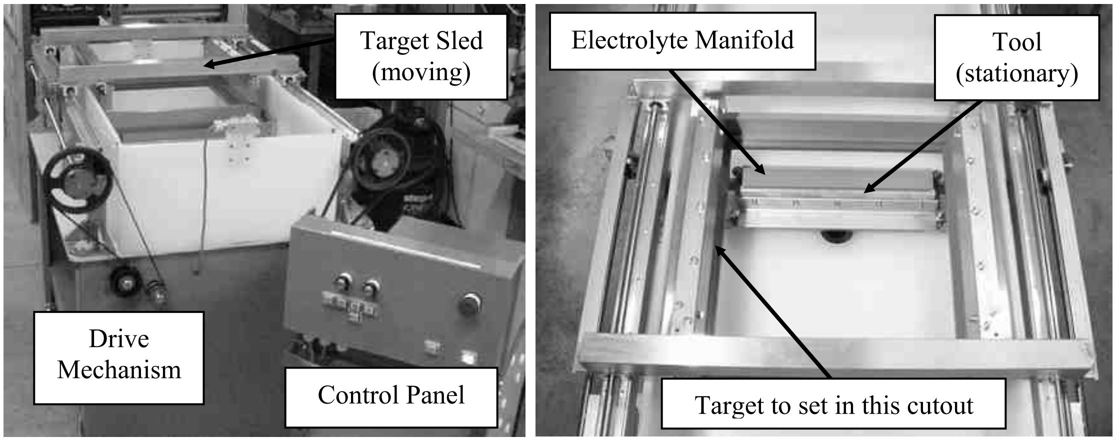


*Figure 2: Titanium Sputtering Target Polishing Station (left), top view (right)*

*Surface Finishing of a Commercially Available Nanocrystalline Steel Coating*

In this project, funded by the US Department of Energy, Faraday is developing a technique to surface finish a nanocrystalline steel coating. This coating is iron based and exhibits extremely high hard characteristics (>15 GPa) and is stable even at temperatures exceeding 650°C.[11] The feasibility study was conducted using carbon steel coupons with a 30 mil coating applied via a high velocity, oxy-fuel (HVOF) thermal spray process. The thermal spray process, however, cannot provide the demanding dimensional accuracy and surface finish necessary for applications such as internal combustion engine components, which are the primary focus of this study. The objective of this project is to enable the widespread use of this coating by providing the means to finish the coating beyond industrial requirements of both dimensional control and surface finish. By introducing this coating into the design of internal combustion engine components, the allowable operating temperature could be increased, resulting in higher fuel efficiency.

 

The apparatus used for the feasibility study is the parallel plate fixture shown in Figure 3. The mean starting surface roughness of the coupons procured from the powder manufacturer was 6.8 µm (270µin) Ra. Using a simple, water based electrolyte, this surface roughness has been reduced to 0.62 µm (25µinch) Ra, an improvement of approximately 10 times. The processing time for this

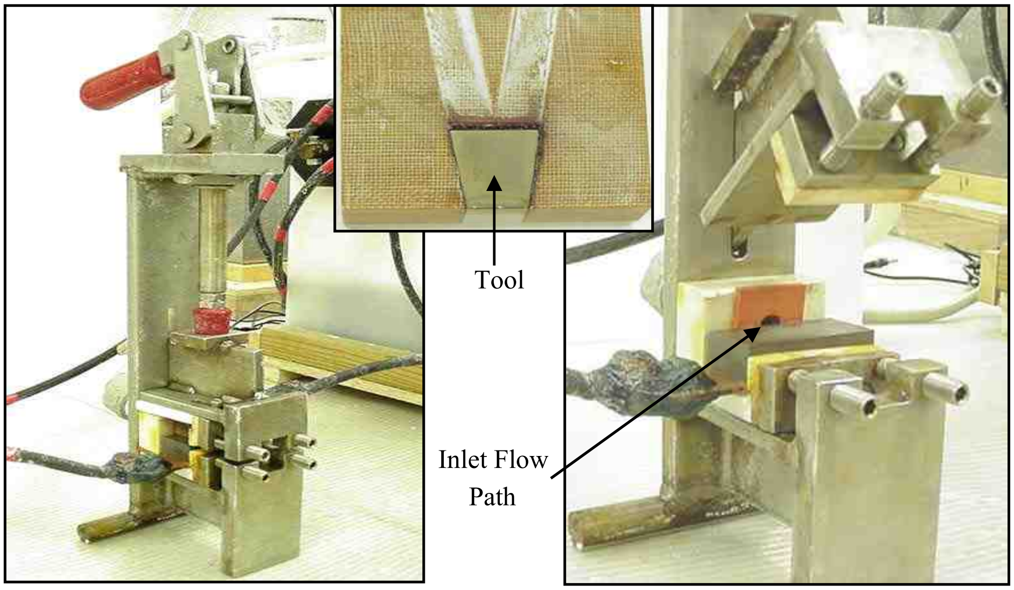


*Figure 3: Parallel Flow Surface Finishing Fixture: (left) assembled view, (center) tool, and (right) coupon loading position*

result was approximately 30 seconds. Current efforts are looking to further improve these results, possibly through the utilization of multiple, sequential waveforms.

*Non-Contact/Zero-Stress Polishing Process for Cu/low-k Semiconductor Applications*

In this project funded by the National Science Foundation, Faraday is developing a non-contact method to planarize semiconductor wafers as a replacement for chemical mechanical planarization (CMP) techniques. This non-contact process will be an enabling technology for the development of Cu/low k semiconductor applications where current CMP technology is not applicable. The objective of the feasibility study is to show that through the proper selection of waveform parameters the copper overplate can be removed without adversely affecting the copper features beneath the overplate or leaving behind "islands" of copper that would interfere with the subsequent layering process. The apparatus developed for the feasibility study is shown in Figure 4. Figure 5 shows some of the results achieved in the feasibility study. The photograph in the upper left corner shows a copper clad laminate in the as received condition. The lower left photograph is the surface after finishing. This photograph shows that the copper cladding was removed to expose the laminate surface in all areas except where it filled a crevice

in the laminate material. The copper remaining in the crevices are dimensionally representative of wafer features. The photograph on the right shows the surface appearance after finishing, which confirms that the surface has been planarized without removing the copper features.

 

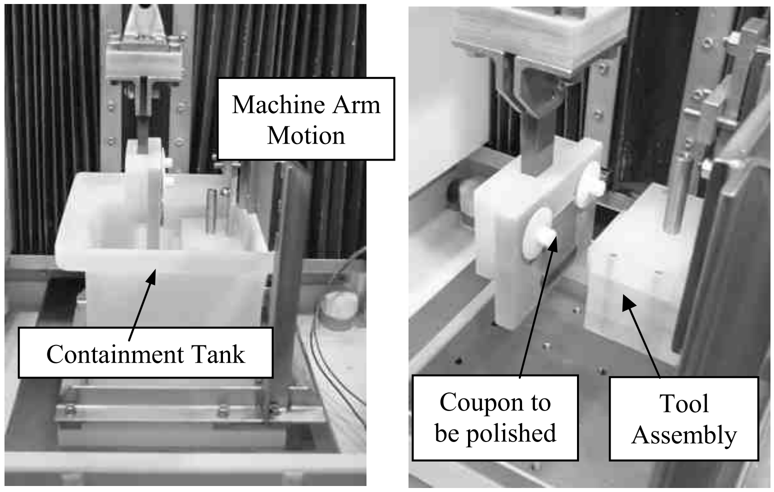


*Figure 4: (Left) Photograph of the Feasibility Study Apparatus, (Right) zoomed view without tank*

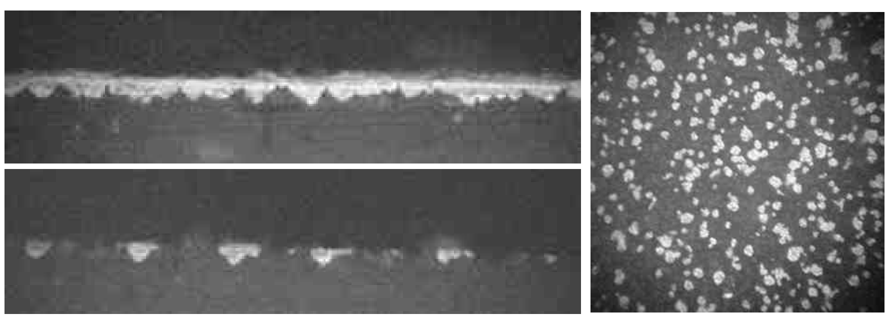

*Figure 5: (left, top) Copper clad laminate prior to finishing (left, bottom) after finishing, and (right) surface appearance after finishing*

*Electrically Mediated Hole Drilling*

This project is in the early stages of feasibility at Faraday. The main objective of the project is to develop an electrically mediated process to drill holes in various materials, including 300 series stainless steel and the nanocrystalline steel coating described previously in this paper. Initially, holes with an approximate diameter of 2 mm with aspect ratios exceeding 3 have been machined; however, a full investigation into the capabilities of the process, including minimum diameters, maximum aspect ratios, and maximum feed rate are planned.

## Conclusions

Reported work has shown the capability of electrically mediated processes for edge and surface finishing of aluminum alloys, titanium alloys, and stainless steel.

Ongoing work is investigating the feasibility and expanding capability of electrically mediated processes to surface finish pure titanium, to finish nanocrystalline steel coatings, to remove copper overplate on semiconductor wafers without removing copper from the underlying tenches, and drill holes.

In summary, the electrically mediated finishing process is a robust process for surface finishing a variety of metal alloys, especially hard passive alloys including titanium, stainless steel, and aluminum alloys.

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