

Breaking the Chemical Paradigm in Electrochemical Engineering: Case Studies and Lessons Learned from Plating to Polishing

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1 Introduction

In his seminal work titled The Structure of Scientific Revolutions [1], history of science philosopher Thomas Kuhn discusses scientific progress and introduces the concept of “paradigms”. Since Kuhn’s work, the use of the word paradigm has dramatically increased without a clear understanding of its meaning [2]. Specifically, a paradigm is not the same as a hypothesis or the scientific method. Simply stated, scientific paradigms are universally recognized concepts providing a framework of assumptions, methods and ways of thinking by a community of practitioners. As such, scientific paradigms are open-ended, providing the tools for a community of scientists, engineers and technologists to solve new problems within their particular field of endeavor. The resulting successful application of the scientific paradigm towards solving emerging scientific, engineering and technological problems further strengthens the paradigm within the community of practitioners, and increases the number of practitioners advocating the paradigm.

However, with the establishment of a scientific paradigm, the community of practitioners often discounts observations that do not conform to the accepted paradigm. As a consequence, peer reviewed manuscripts and grant proposals building on non-conforming observations often go unpublished and unfunded, respectively. Kuhn summarizes this evolving state of affairs by noting that scientific, engineering and technological advancement based on established paradigms [3]

“...does not aim at novelties of fact or theory and when successful, finds none.”

In essence, the entrenched scientific community becomes so reliant on the established paradigm that observations that do not conform to the paradigm are ignored or discounted.

In summary, paradigms provide the basis for scientific discovery and engineering and technological advancements while simultaneously suppressing non-conforming observations that could lead to new or modified paradigms. In this contribution, events at Faraday Technology, Inc. spanning a period of approximately twenty-two years (1991 to 2013) are described that led to the development of an industrially compatible electropolishing process for niobium superconducting radio frequency (SRF) cavities using pulse reverse voltage waveforms in conjunction with low concentration aqueous acid electrolytes devoid of hydrofluoric acid. This development is a paradigm-shift from the widely accepted viscous salt film electropolishing model of Jacquet [4].

One of the authors’ objectives is to report the specific technical discoveries and observations that led to an environmentally benign and industrially compatible pulse reverse voltage electropolishing process for SRF cavities. While acknowledging that scientific, engineering and technological advances occur by building on well-established paradigms, another of the authors’ objectives is to provide useful insights related to the pursuit of non-conforming observations that can lead to potentially paradigm-shifting technologies. The authors conclude that scientific discovery of paradigm-shifting innovations require a careful balance between current

fundamental understandings combined with the pursuit of observations that do not necessarily fit the existing paradigm.

1.1 Perspective

The authors' perspective is based on over 20 years of experience at a small research, development and engineering company, that was founded in 1991 to conceive, develop and commercialize novel electrodeposition/plating technologies based on pulse current/pulse reverse current (PC/PRC) electrolytic principles. Historically, progress in the plating industry has focused on a reliance on "electrochemical art" of chemical additives, which is perpetuated by chemical suppliers acting as "gate keepers" to the metal finishing industry. Specifically, the current reliance on electrochemical art may be traced to approximately one hundred and fifty years ago when the understanding of electrochemical principles was nascent. Plating history is full of stories documenting the serendipitous "discovery" of chemical additions to plating baths leading to the desired coating properties. These discoveries ultimately served as models for development of new plating bath chemistries, which led to the proprietary chemical additives of today's chemical formulators. While considerable progress was made using this chemical paradigm, possible solutions that did not involve additives were deemphasized. By shifting the paradigm from the "electrochemical art" of chemical additives to the electrochemical science of nucleation, growth, kinetics and mass transport phenomena, the authors speculated that pulse reverse waveforms could be utilized to develop robust and environmentally benign metal finishing processes, while retaining the advantages of electrodeposition based on chemical additions such as high deposition speed and low capital investment.

The company's mission is to conceive and commercialize electrochemical processes based on the PC/PRC technology platform. To support these activities, funding is obtained through the highly competitive U.S. Small Business Innovative Research (SBIR) and Small Business Technology Transfer (STTR) programs. These programs consist of a Phase I technology feasibility demonstration activity of approximately \$70,000 to \$150,000 for six- to twelve-months period of performance. Approximately 10% of the Phase I proposals are awarded. After the successful conclusion of an awarded Phase I program, the small business may then apply for Phase II technology validation funding of \$300,000 to \$1,000,000 for duration of two years. The Phase I to awarded Phase II conversion rate is approximately 30%, effectively making the "odds" of receiving Phase II funding one in thirty. Because of the emphasis on innovation in seeking highly competitive SBIR/STTR funding, small business researchers must often look outside traditional scientific paradigms both in the proposal phase and while gathering data that demonstrates the proof of concept of their proposed technology. However, these observations generally must be tempered with acknowledgement of the traditional scientific paradigms, especially given that proposal reviewers may base their evaluation on their knowledge and acceptance of those traditional paradigms.

Once the Phase II development activity has been completed, additional funding to commercialize the technology for private sector use or to transition the technology for government use comes from other sources of private sector or non-SBIR government funding, respectively. While the SBIR/STTR programs represent a highly competitive source of technology demonstration and validation funding, importantly these programs allow the small business to retain assignment of the inventions "conceived or first actually reduced to practice" with said funds [5].

The company considers itself to be an "innovation factory" based on its pulse/pulse reverse electrolytic technology platform, and its product is intellectual property in the form of know-how, trademarks and patents.

Strategic partners fund the pre-production α -scale validation of the subject technology with the option to acquire the competitive advantage associated with the intellectual property relevant to the technology. Generally speaking, the strategic partner does not require a detailed mechanistic understanding of the technology. However, the strategic partner does require sufficient understanding to enable implementation and robust process control of the technology. This experience is similar to that reported for the development of the nickel-iron plating process for thin film head production, which was in production years before [6]

“...a satisfactory mechanism of the phenomena had been achieved.”

The competitive advantage associated with the technology is generally provided to the strategic commercial partner in the form of “field-of-use licenses”, “early adapter licenses”, or “supply chain licenses”, although patents are sometimes sold [7]. In the case of governmental strategic partners the technology is freely available without the need for acquiring the rights to the patents and/or know-how [5]. In summary, the company’s business model utilizes “seed” funding to advance the pulse/pulse reverse electrolytic platform technology via the highly competitive SBIR/STTR environment, identifying university collaborators as appropriate, engaging commercial and governmental strategic partners and establishing intellectual property in the form of patents and know-how.

In order to provide a complete picture of this approach, this chapter will begin the discussion by exploring some initial successes in pulse reverse plating of copper. As will be discussed below, a paradigm-shift was identified in the process for deposition of copper, specifically with respect to the conventional reliance on additive chemistries to achieve the desired deposit characteristics. This recognition that the use of pulse reverse electric fields may obviate the need for chemical additives in cathodic (electrodeposition, plating) technologies was later applied to a wide range of anodic (electrochemical deburring, electrochemical machining, and electropolishing) technologies, to enable performance based processes using environmentally benign and worker safe electrolytes. Although not discussed further, pulse reverse electrolytic principles have also been applied to facilitate electrophoretic deposition from electrolytes containing higher water contents than permitted in DC electrophoretic deposition [8,9].

Consequently, while the company’s initial founding vision was:

*“...to change the focus of **electrodeposition processes** from the use of electrolytes with multicomponent chemical additions to the use of simpler electrolytes enabled by pulse current/pulse reverse current electric fields...”*

This vision has evolved to include PC/PRC anodic dissolution or surface finishing processes such as deburring, electrochemical machining, electropolishing and electrochemical through-mask etching. This broadening of the vision was based on observations and speculations that the lessons learned from cathodic PC/PRC electrodeposition processes could be adapted to anodic PC/PRC surface finishing processes. Consequently, the current company vision is:

*“...to change the focus of **electrochemical manufacturing/engineering processes** from the use of electrolytes with multicomponent chemical additions to the use of simpler electrolytes enabled by pulse current/pulse reverse current electric fields...”*

This vision has led to approximately thirty U.S. patents as well as foreign patents covering various embodiments of pulse/pulse reverse electrochemical processes as well as electrochemical apparatus. In addition, some of the technical successes have been recognized with awards including the Blum Scientific Achievement award, a 2011 R&D 100 award, and a 2013 Presidential Green Chemistry Challenge award.

2 A Brief Overview of Pulse Reverse Current Plating

The concept of pulse reverse current plating is not new and was first reported at least in the early part of the nineteenth century [10]. The guiding principles of pulse current and pulse reverse current plating, presented in 1986 in the classic compendium *Theory and Practice of Pulse Plating* edited by Jean-Claude Puipe and Frank Leaman, are still relevant today [11]. In spite of numerous theoretical and experimental studies characterizing pulse current plating reported in the 1970s (these will be briefly summarized below), most of the studies directed towards practical applications of PC/PRC plating used the existing plating baths containing chemical additions optimized for direct current (DC) plating. Regarding the practical applications of PC/PRC plating, two questions guided the pursuit of novel PC/PRC electrodeposition technologies:

1. Why should one expect that plating bath chemical additives optimized for DC plating would be optimum for PC/PRC plating?
2. Compared to DC plating, can PC/PRC enable plating from a simpler plating baths with low or no chemical additives and thereby lead to a more robust plating process?

A brief review of pulse current plating is provided to establish the basis for evolving plating and metal finishing activities, ultimately leading to the development of the niobium electropolishing process in low viscosity solutions. This discussion, while perhaps technically dry, sets the stage by outlining the guiding principles that enabled us to design waveforms for the specific applications described later. A more recent review of pulse current plating is also available [12].

Fig. 1 presents a generic pulse reverse current waveform for a net cathodic or plating process. The generic description illustrates a cathodic (forward) pulse followed by an off-time, followed by an anodic (reverse) pulse and followed by a second off-time. The cathodic peak current density (i_{cathodic}), cathodic on-time (t_{cathodic}), cathodic off-time ($t_{\text{off,cathodic}}$), anodic peak current density (i_{anodic}), anodic on-time (t_{anodic}), and anodic off-time ($t_{\text{off,anodic}}$) are individual variables for process control. There are numerous embodiments of pulse and pulse reverse current waveforms [13], a common one being waveforms consisting of only cathodic pulses. Additionally, other common embodiments that include the anodic pulse may eliminate one or both off-times.

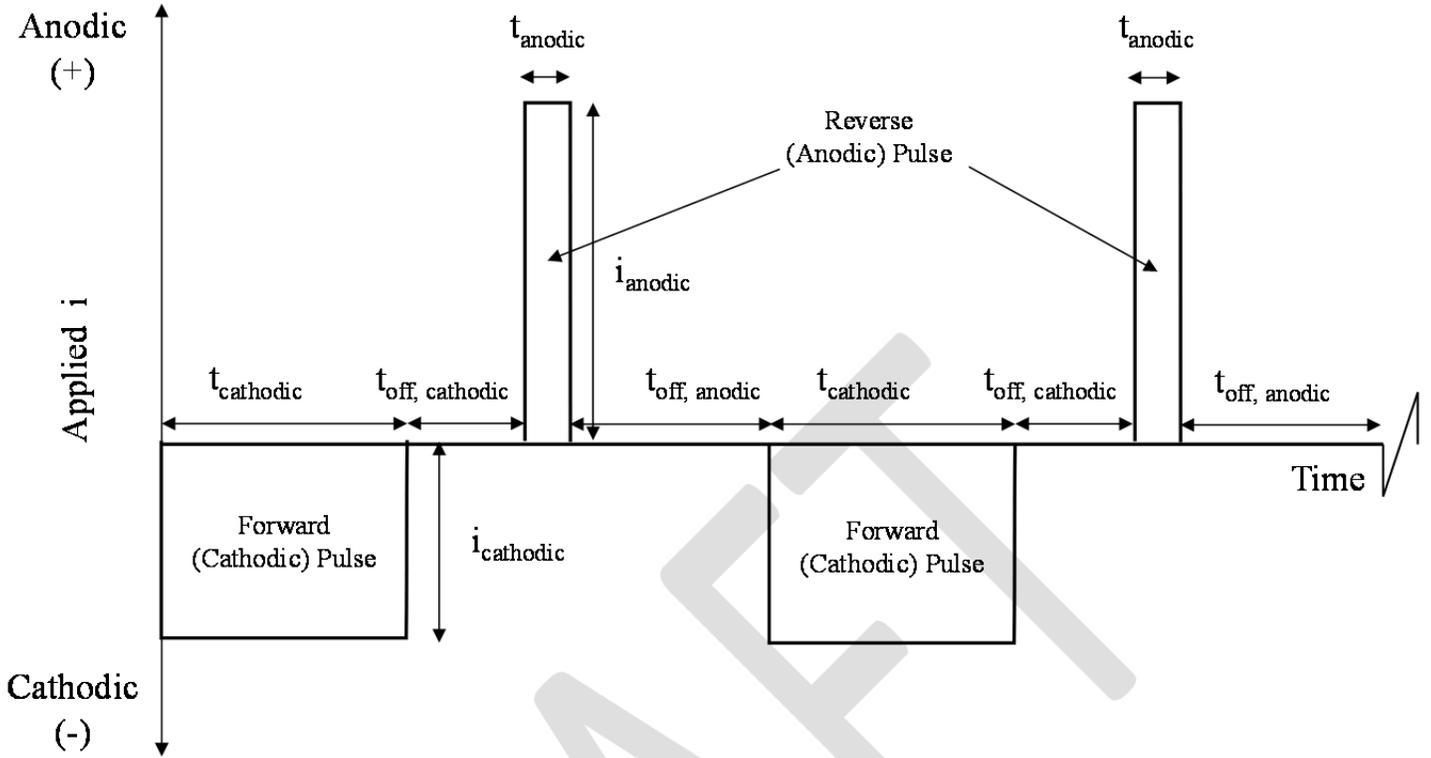


Fig. 1. Schematic illustration of a generalized pulse reverse current waveform.

The sum of the cathodic on-time, anodic on-time, and off-time(s) is the period (T) of the pulse and the inverse of the period is the frequency (f). Specifically,

$$T = (t_{\text{cathodic}}) + (t_{\text{off,cathodic}}) + (t_{\text{anodic}}) + (t_{\text{off,anodic}}) \quad (1)$$

$$f = (1/T) \quad (2)$$

The cathodic duty cycle (γ_{cathodic}) is the ratio of the cathodic on-time to the pulse period, and the ratio of the anodic on-time to the pulse period is the anodic duty cycle (γ_{anodic}). The frequency and duty cycles are additional variables for process control. The average current density (i_{average}) or electrodeposition rate is given by:

$$i_{\text{average}} = (i_{\text{cathodic}})(\gamma_{\text{cathodic}}) - (i_{\text{anodic}})(\gamma_{\text{anodic}}) \quad (3)$$

It should be noted that even though pulse current and pulse reverse current (PC/PRC) waveforms contain off-times and anodic periods, the plating rate is typically the same or higher than in direct current plating. As discussed below, this is attributed to the fact that the “instantaneous” peak currents attained during the pulse on-time can be much higher than that attained during DC plating.

2.1 Mass Transport Effects in Pulse Current Plating

Mass transport in pulse current plating is a combination of steady state and non-steady state diffusion processes [14]. The mass transfer limited current density (i_l) is related to the reactant concentration gradient ($C_b - C_s$) and to the diffusion layer thickness (δ) by:

$$i_t = -nFD (\partial C/\partial x)_{x=0} = -nFD[(C_b - C_s)/\delta] \quad (4)$$

where n , F , D are the number of equivalents exchanged, Faraday's constant, and diffusivity of the reacting species, respectively. In DC electrolysis, δ is a time-invariant quantity for a given electrode geometry and hydrodynamic condition. In pulsed electrolysis, however, δ varies from 0 at the beginning of the pulse to its steady state value when the Nernst diffusion layer, δ_N , is fully established [15,16,17]. The corresponding mass transport limiting current density is equal to an infinite value at $t = 0$ and decreases to a steady state value of the DC limiting current density. The advantage of pulse electrolysis is that the current is interrupted before δ reaches steady state, allowing the reacting ions to diffuse back to the surface and partially or completely replenish the surface concentration to its original value before the next current interruption. Therefore, the concentration of reacting species in the vicinity of the electrode changes with the pulse frequency. During pulse electrolysis, Ibl [18,19] proposed a "duplex diffusion layer" consisting of a pulsating layer, δ_p , and a stationary layer, δ_s for a deposition process (Fig. 2a). Fig. 2b shows the equivalent diffusion layers for an anodic process, e.g. metal removal.

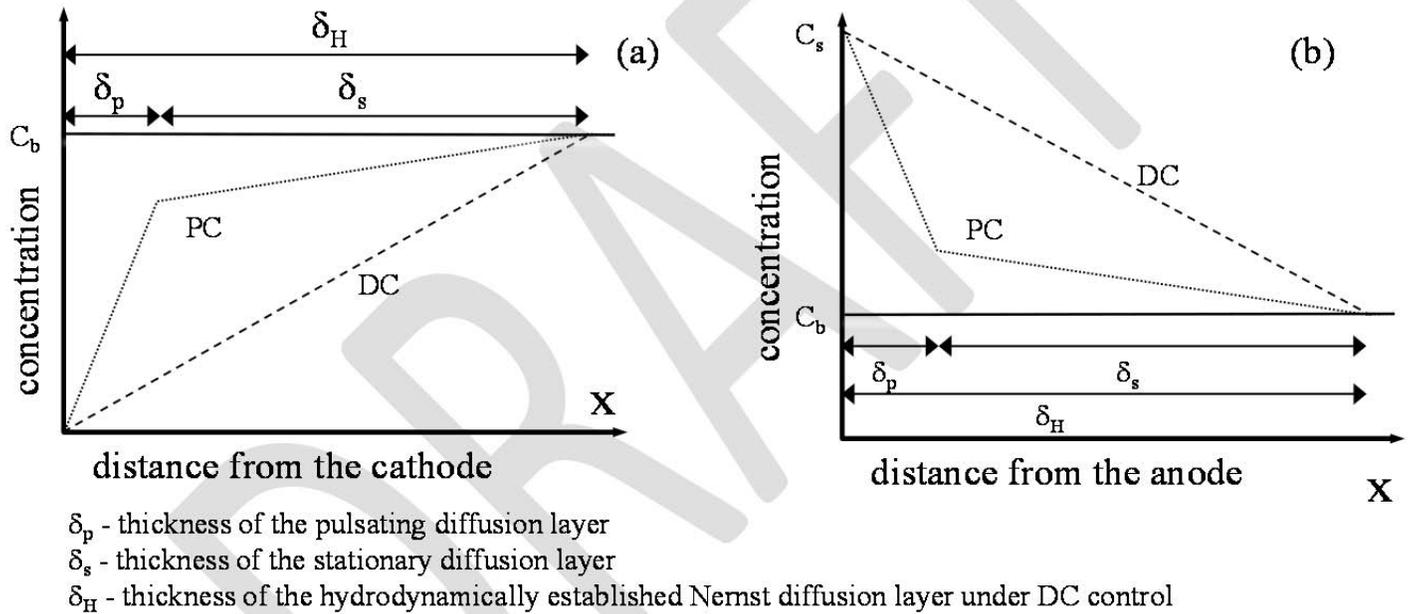


Fig. 2. Schematic representation delineating the pulsating versus stationary diffusion layer for (a) a cathodic (metal deposition) process, and (b) an anodic (metal removal) process.

By assuming a linear concentration gradient across the pulsating diffusion layer and conducting a mass balance, Ibl derived the pulsating diffusion layer thickness (δ_p) as:

$$\delta_p = (2Dt_{on})^{1/2} \quad (5)$$

where t_{on} is the pulse on-time. When the pulse on time is equal to the transition time, the concentration of reacting species at the interface drops to zero at the end of the pulse. An expression for the transition time, τ , is:

$$\tau = ((nF)^2 C_b^2 D) / 2i_c^2 \quad (6)$$

More exact solutions are given by integrating Fick's diffusion equation:

$$\delta_p = 2((Dt_{on})/\pi)^{1/2} \quad (7)$$

$$\tau = \pi((nF)^2 C_b^2 D)/4i_c^2 \quad (8)$$

Fig. 3 shows the change in pulsating diffusion layer thickness as a function of the pulse on-time. For on-times less than the transition time, τ , the concentration of the reacting metal species at the interface remains above zero. For on-times equal to or greater than τ , the concentration of the reacting metal species at the interface is zero, and the process is mass transport limited. For a DC process, a hydrodynamic Nernst diffusion layer is established.

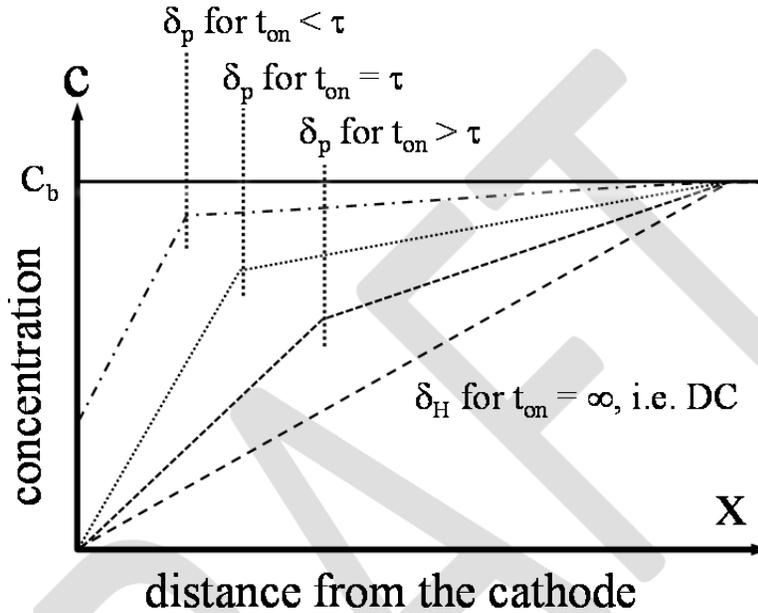


Fig. 3. Schematic representation of the change in pulsating diffusion layer thickness as a function of the relationship between t_{on} and the transition time, τ .

Yin [20] derived a similar relationship for the pulsating diffusion layer in the case of pulse reverse current plating. To emphasize that the thickness of the pulsating diffusion layer is related to the pulse current on-time, this is referred to as the “electrodynamics” diffusion layer. The key points used in the development of a pulsed process for electrodeposition are: (1) the electrodynamic diffusion layer thickness is proportional to pulse on time and (2) transition time is inversely proportional to the pulse current.

2.2 Current Distribution Effects in Pulse Current Plating

Current distribution and hence metal distribution are also a function of the pulse current plating parameters [21,22]. Current distribution is an important parameter in coating electrodeposition. Primary current is governed solely by the geometric effects of the plating apparatus. Secondary current distribution is governed by kinetic effects and activation overpotentials are considered. Tertiary current distribution is governed by mass transport effects and both activation and concentration overpotentials are considered [23]. The addition of secondary or tertiary current distribution effects tend to make the current distribution more uniform, as compared to primary current distribution alone.

For the purposes of this discussion, it is helpful to examine the balance of primary and secondary current distribution in terms of the Wagner number. The Wagner number (W_a) is the ratio of the activation polarization (kinetic effects) to the ohmic polarization (geometric effects):

$$W_a = (d\eta/di) \cdot (\kappa/l) \quad (9)$$

where “ $d\eta/di$ ” is the Tafel slope for the reaction of interest, “ κ ” is the solution conductivity, and “ l ” is the characteristic length over which the electrochemical reaction is assumed to take place. For $W_a \ll 1$, primary current distribution prevails and the current distribution is less uniform. For $W_a \gg 1$, secondary current distribution prevails and the current distribution is more uniform. According to the Wagner number relationship, the tools with which to understand and perhaps manipulate the balance of primary, secondary and tertiary current distribution are:

- Tafel slope
- Solution conductivity
- Characteristic length

The characteristic length, l , may change over time as a surface is roughened or smoothed. The solution conductivity is a function of electrolyte chemistry and temperature. Manipulation of the Tafel slope may be done using pulsed electric fields.

The work of Prof. Der-Tau Chin’s group at Clarkson University related to selective plating of solder and gold bumps helps to understand the effect of pulsed currents on the Tafel slope [24]. Solder and gold bumps are used as lead frame contacts in the electronics industry. The bumps need to be a certain height, l (the characteristic length in the Wagner equation), in order to effectively function as a lead frame contact. The electronics industry desired to achieve the required height with minimum spreading of the bump in order to conserve lead frame “real estate” and material cost. Modeling and experimental studies were conducted of bump plating under DC and PC conditions at the same average current densities [24]. Using the geometrical setup in Fig. 4, they reported that by decreasing the duty cycle during pulse current plating, the spread of the bump was reduced for a constant height. The results were rationalized in that during pulse current plating the “time-averaged” Tafel slope was reduced compared to DC. Consequently, W_a trended towards being much less than 1, and therefore the current distribution was less uniform.

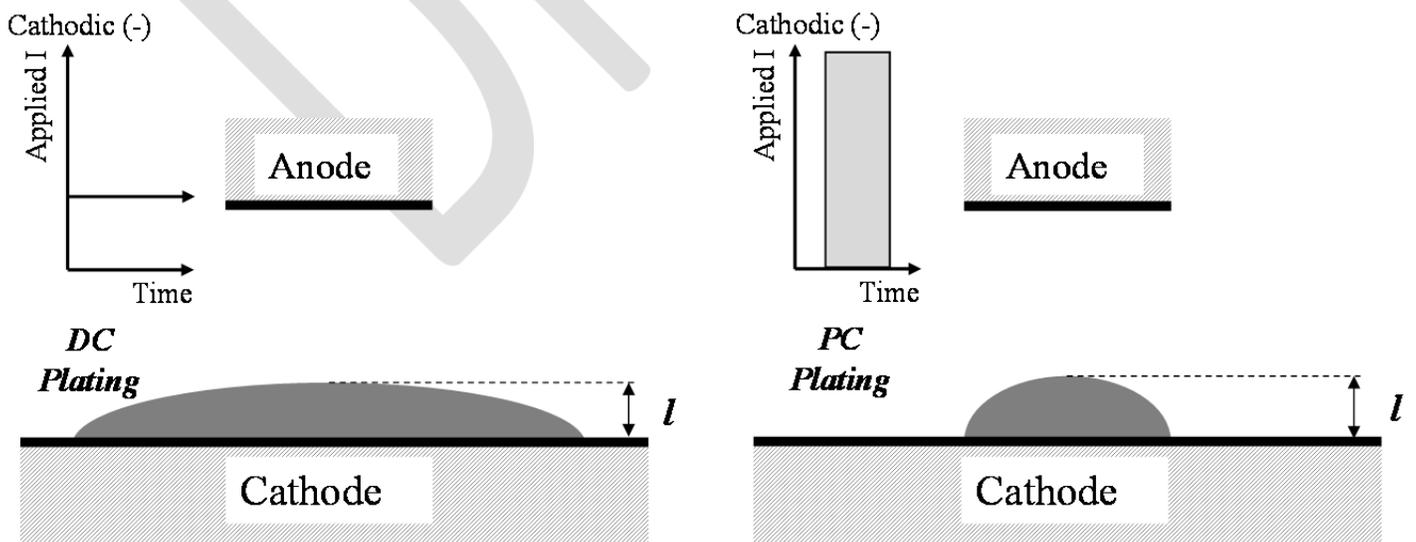


Fig. 4. Schematic illustration of “bump” plating under DC and PC conditions at the same average current density.

A further consideration with regard to current distribution and the balance of primary, secondary and tertiary effects is the relationship between the characteristic length, l , and the diffusion layer. In a macroprofile (Fig. 5a), the roughness of the surface is large compared with the thickness of the hydrodynamic diffusion layer, δ_H , and when a pulsed electric field is applied, the diffusion layer is compressed to form a pulsating or electrodynamic diffusion layer, δ_p . The pulsating diffusion layer, δ_p , tends to follow the surface contour, and becomes more compressed and thinner as the pulse on-time becomes shorter. In a microprofile (Fig. 5b), the roughness of the surface is small compared with the thickness of the hydrodynamic diffusion layer, δ_H . In this case, for a long pulse on-time, the pulsating diffusion layer is compressed, but still is much larger than the characteristic length, and the microprofile is maintained. For very short pulse on-times, the pulsating diffusion layer is compressed to the point at which it follows the surface contour, and the system effectively mimics a macroprofile.

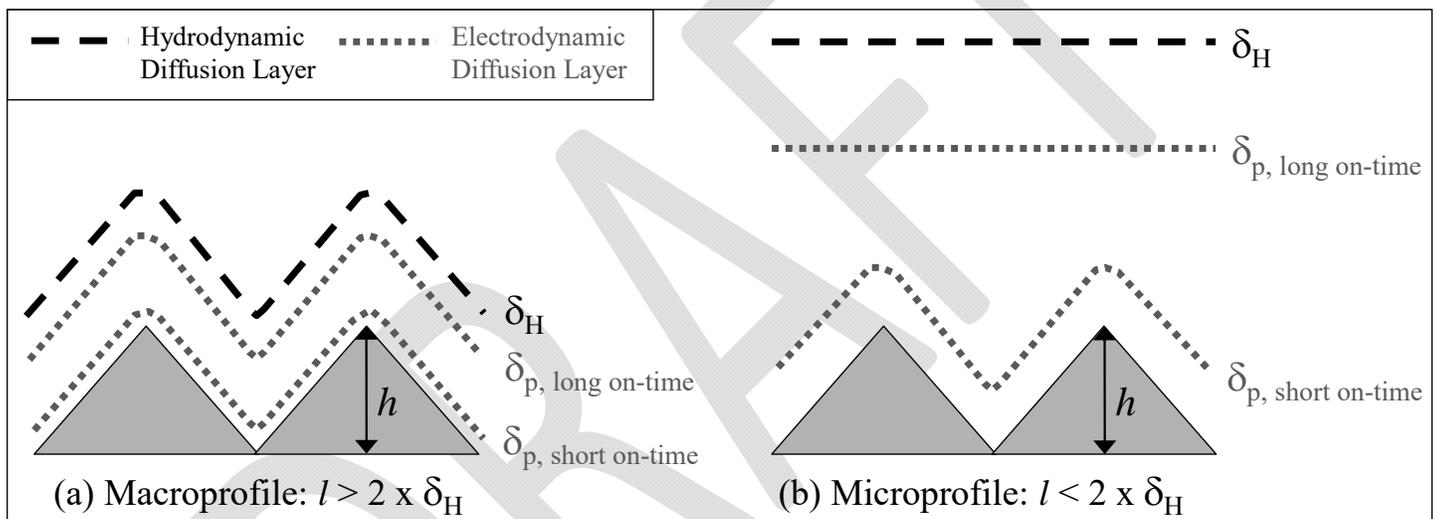


Fig. 5. Schematic illustration of a) macroprofile and b) microprofile.

A final consideration is that if the applied waveform is designed such that the pulse on time is much longer than the transition time, tertiary current distribution will play an important role in the process. With the addition of tertiary control, the concepts of macroprofile and microprofile and their influence on current distribution become important.

Under DC conditions and mass transport control, a macroprofile results in the most uniform current distribution and a nearly conformal deposit. As illustrated in Fig. 5a, the application of pulse currents generates a smaller macroprofile. Based on experimental observations, for a macroprofile boundary layer condition, relatively long pulse on-times can yield a slightly non-uniform current distribution compared to DC conditions, and relatively short pulse on-times can yield a significantly more non-uniform current distribution than DC conditions. Assuming the same average current, for shorter pulse on-times the relative influence on current distribution shifts from tertiary current distribution control to secondary as well as primary current distribution control. Consequently, as concentration polarization effects are removed, the current distribution becomes less uniform.

These observations are consistent with Prof. Chin's work [24] under a macroprofile where they observed a more non-uniform deposit with shorter pulse on-times.

Under DC conditions and mass transport control, a microprofile results in the most non-uniform current distribution and a non-conformal deposit. As illustrated in Fig. 5b, the application of pulse currents with a small enough on-time can convert a microprofile to a macroprofile, establishing a small δ_p [Eqn. 5]. For a microprofile diffusion layer condition, assuming tertiary current distribution control is maintained, short pulse on-times sufficient to convert the microprofile to a macroprofile results in a significantly more uniform current distribution. Conversely, long pulse on-times sufficient to maintain the microprofile results in a slightly more uniform current distribution compared to DC, assuming tertiary control is maintained by selecting on-times and peak currents that ensure $t_{on} \gg \tau$ per Eqns. 6 and 8.

Consequently, by applying the appropriately designed current pulse in terms of peak current and on-time, the current distribution can be effectively focused or de-focused to create more uniform or more non-uniform deposition, respectively. This enhanced process control, enabled by the additional parameters associated with pulse processes relative to DC, is especially attractive for complex shaped substrates requiring uniform coatings. Since these concepts are based on the influence of pulse currents on current distribution, they are applicable to metal deposition and well as metal dissolution.

There are four pulse types, independent of anodic or cathodic orientation, that can be used to tailor waveforms for specific applications, and these are summarized in Fig. 6. While there are additional permutations that may be considered, these are the ones that have proven most useful in the development activities to date.

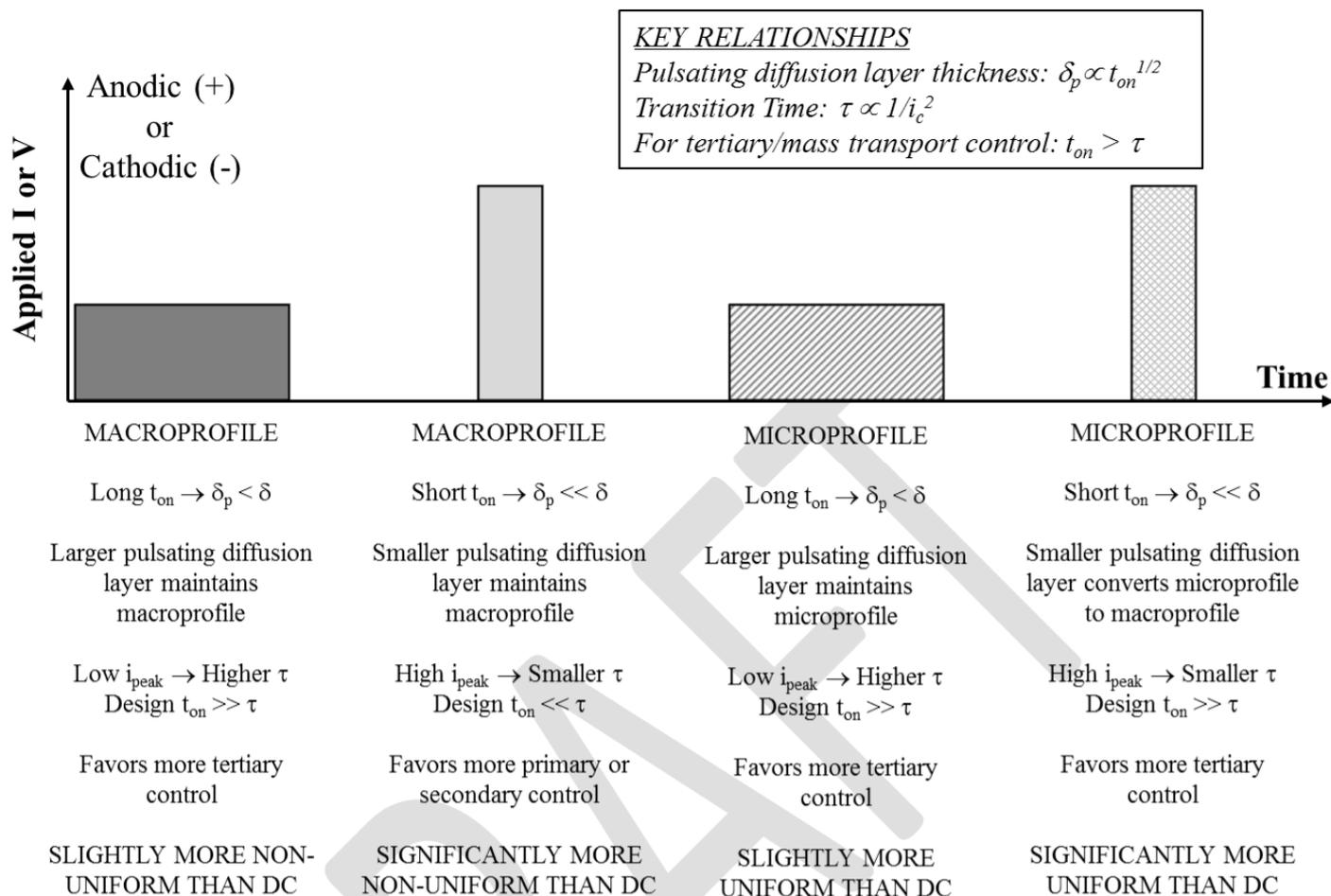


Fig. 6. Guidelines for designing pulse parameters as a function of macroprofile/microprofile and need for more uniformity or more non-uniformity.

To summarize, while the Wagner number is not being used to directly design the pulse waveform parameters, the principles involved are being used to be cognizant of the effect of both the characteristic length and how the pulse parameters change the Tafel slope on the balance of primary and secondary as well as tertiary current distribution. That knowledge can be combined with an understanding of electrochemical processes operating under either macro or microprofile boundary layer conditions to design the pulse parameters to achieve more uniformity or non-uniformity in each process, whether it be metal deposition or metal removal. These are guiding principles only, based on a review of the literature combined with experimental observations, and some iteration is generally required to determine appropriate peak currents and voltages and on-times. It has proven challenging to date to assign exact numerical values for these parameters *a priori*, though numerical simulations may be used in the future to achieve predictive capabilities.

For electrochemical processes which are close to 100% faradaic efficiency for both metal deposition and metal dissolution, combining these cathodic and anodic pulses can create net waveforms that will achieve the overall desired process result. Combining multiple waveforms into sequences may also be required, as will be shown in the examples to follow. This is easily done with modern programmable rectifiers – a far simpler change than having to modify electrolytes or electrode geometries to achieve the same effect.

2.3 Grain Size Effects in Pulse Current Plating

Grain size in electrodeposited coatings, and hence mechanical properties such as ductility, is also a function of the pulse current plating parameters [25]. During the plating process, as ions enter the electrified interface between the solution and the cathode, a charge transfer reaction results in the formation of adatoms on the surface of the cathode. Electrocrystallisation is the mechanism by which adatoms are incorporated into a crystal lattice during plating. Electrocrystallization can occur by either growth on previously deposited crystals or nucleation of new crystals. If electrocrystallization occurs by growth on previously deposited crystals, the resulting deposit will consist of large grains. In contrast, if electrocrystallization occurs by nucleation of new crystals, the resulting deposit will consist of small grains or even amorphous deposits. The nucleation rate (v) is given by:

$$v = k_1 \exp(-k_2/|\eta|) \quad (10)$$

where k_1 is proportionality constant, k_2 is related to the amount of energy needed for the two-dimensional nucleation, and η is the overpotential. The nucleation rate increases exponentially with increasing overpotential.

Pulse current plating generally utilizes peak current densities that are much higher than the current densities used in DC plating [15]. Therefore, the instantaneous current or voltage pulses, and hence the overpotentials during pulse current plating, may be higher than during DC plating. Consequently, pulse current plating can promote nucleation and a finer grained structure compared to DC plating. In fact, the “grain size” concept has been taken to the extreme by forming 4 to 5 nm catalyst particles for gas diffusion electrode applications [26,27,28]. Numerous studies have reported the effect of increased current density on grain size during pulse current plating [11]. These investigations included 1) increasing the pulse peak current density while maintaining a constant pulse on-time and average current density, as illustrated in Fig. 7a, and 2) increasing the pulse peak current density while maintaining a constant average current density with a shortened on-time, as illustrated in Fig. 7b. In the methodology illustrated in Fig. 7a, the cathodic charge per pulse and off-time as well as the pulse peak current density are increased. In the methodology illustrated in Fig. 7b, the off-time is increased slightly as the pulse peak current density is increased, while the cathodic charge per pulse is maintained. In both cases an increase in pulse peak current density resulted in a deposit with smaller grain sizes, even though the total charge for each waveform remained the same. Finally, the pulse on-time and pulse off-time also affect the grain size of the deposit during pulse current plating. The impact of pulse on-time and off-time is more complicated and is generally dependent on the presence or absence of species in the plating bath that inhibit or promote grain growth.

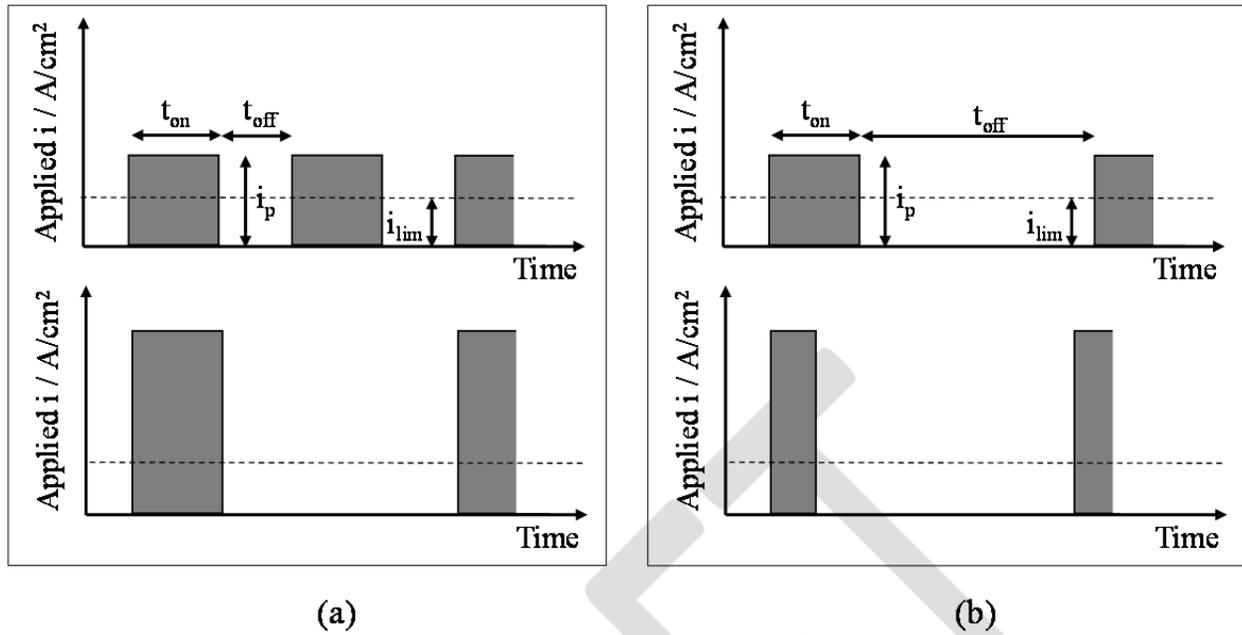


Fig. 7. Illustration of two methodologies for studying the impact of increasing pulse peak current density on grain size while maintaining the same average current density, (a) cathodic charge per pulse and off-time increase, (b) cathodic charge per pulse and off-time are constant.

2.4 Current Efficiency Effects in Pulse Current Plating

Current efficiency during electrodeposition is also a function of the pulse current plating parameters [29]. As is well known in the plating art, hydrogen evolution occurs during plating of many materials. The fraction of total current attributed to the desired metal deposition reaction is termed the current efficiency. Often, low current efficiency plating processes adversely impact deposit morphology such as increased porosity and increased crack formation. In addition, the hydrogen evolution reaction inherently increases the pH at the electrode surface even in an acidic plating bath. The current efficiency and hence the property of the deposits can be significantly impacted by pulse current plating parameters such as pulse peak current density, on-time, off-time as well as pulse reverse current parameters.

2.5 Concluding Remarks for Pulse Current Plating

Pulse current and pulse reverse current plating offers considerable parametric flexibility relative to DC plating. Just as there are infinite combinations of height, width, and length to obtain a given volume, in pulse and pulse reverse processes there are unlimited combinations of peak current densities, duty cycles, and frequencies to obtain a given electrodeposition rate [30]. Pulse current plating parameters impact mass transport, current distribution and hence metal distribution, deposit grain size and hence mechanical properties, and current efficiency and hence deposit morphological characteristics. The key challenge is to identify the key PC/PRC waveforms parameters to tune for a specific plating application without initiating an exhaustive experimental development program. The above review suggests that the key waveform parameters are the pulse on-times and pulse peak currents based on their impact on the “electrodynamic” pulsating boundary layer (Eqns. 3 and 5) and the transition time (Eqns. 4 and 6), respectively. While waveform parameters such as duty cycle and frequency are often reported, these parameters are derived from the more physically meaningful pulse peak currents and

pulse on-times. Based on this “tangible” understanding as well as evolving observations, guiding principles have been reported for developing pulse and pulse reverse waveform parameters for specific electrodeposition applications [31].

3 Early Developments in Pulse Plating

In current state-of-the-art metal plating operations, chemical additives are used to produce the desired properties and/or geometry of the metal coating. The additives influence a number of deposit properties, including 1) brightness, 2) hardness, 3) adhesion, 4) corrosion resistance, 5) wear resistance, 6) internal stress, and 7) mechanical characteristics, i.e. strength and ductility. These chemical additives commonly include organic, metallic, ionic, and/or nonionic substances in concentrations ranging from several mg/L to a few percent. The influence of additives is dramatic in that one additive molecule may affect the electrodeposition of several thousand metal ions [32]. During plating the additives are consumed and/or incorporated into the deposit and must be quantified and replenished. The “discovery” of plating additives was patented in 1847 and even Edison experimented with plating additives [33]. Currently, a vibrant industrial sector of chemical formulators has evolved to supply the plating industry with proprietary additives for various applications.

In the mid-1990s, Faraday was approached by the research director of chemical formulator who supplied proprietary additives for copper plating baths used in the printed circuit board (PCB) industry. One of their competitors had implemented a pulse reverse current (PRC) plating process for “plated through-holes” (PTHs) used as z-axis interconnects in the PCB industry. The PRC plating process resulted in more uniform plating of PTHs, as measured by the throwing power. Generally, the throwing power is the ratio of the plated copper thickness on the surface of the PCB to the plated copper thickness in the center of the PTH. The PCB industry specification for throwing power was ~80% and the use of PRC compared to DC copper plating permitted higher current densities and hence higher throughput while maintaining the required throwing power. The chemical formulator funded a “research for hire” activity to demonstrate the benefit of PRC copper plating of PTHs using their proprietary additives. The PTH diameter of interest at that time was 325 μm at an aspect ratio of ~4:1. The initial attempts using the PRC waveform parameters of their competitor resulted in a powdery burnt copper deposit that was unacceptable and consequently throwing power was irrelevant. The fact that slight changes in the proprietary additives of one chemical formulator would not be optimum using the same PRC parameters was not surprising due to the complex impact of PRC parameters on the adsorption/desorption of ionic organic additives during the cathodic and anodic pulse on-times during plating. Using a small design of experiments approach, the PRC parameters that successfully plated bright copper deposits using the client’s proprietary additives were established, with the target throwing power for the PTH at the same current density as reported by the competitor.

In addition, with the PRC waveform parameters identified for the chemical formulator client, the effect of the leveling additive concentration on the throwing power for the PTHs was investigated. Interestingly, as the leveling additive concentration was increased from the specified concentration, the throwing power decreased. Conversely, as the leveling additive concentration was decreased from the specified concentration the throwing power increased. In fact, the throwing power was over 100% for a leveling additive concentration of near zero. In summary, PRC copper plating yielded better throwing power without the leveling additive, than either DC or PRC with the leveling additive! Since providing chemistry without additives was outside the business model of the chemical formulator client, the project was discontinued. In spite of the lack of interest in moving forward,

this outcome was encouraging in that it showed the potential to realize the company vision of using PRC processing to enable simpler plating bath chemistries for an industrially important application.

3.1 Leveling without Levelers using Pulse Reverse Current Plating

Due to the need for increased packing density, the PCB industry has been continually driven to incorporate smaller z-axis interconnect features alongside the larger PTHs. These features include microvias of $\sim 100\ \mu\text{m}$ diameter and smaller. Researchers had attempted to plate copper into $100\ \mu\text{m}$ microvias using pulse reverse waveform parameters that had been previously been employed to plate PTHs of $>200\ \mu\text{m}$. These waveforms were applied in conventional plating baths containing the typical chemical additions; the existing paradigm for copper plating in the electronics industry focuses first on the impact of chemistry on the process, and latterly on the impact of the electric field parameters.

Based on the prior experience and observations with the chemical formulator, which suggested that a new paradigm of predominantly electric field process control may be emerging, it was felt that the challenge of plating both these new z-axis interconnect features as well as the larger PTHs could be addressed in simple copper plating baths without the addition of brighteners and levelers, using specifically tailored pulse reverse electric fields. The boundary layer in a typical PCB plating tank was estimated to be approximately 50 to $75\ \mu\text{m}$. Essentially, any feature with an asperity greater than approximately two times the boundary layer thickness would be plated under a macroprofile condition and any feature with an asperity less than approximately two times the boundary layer would be plated under a microprofile condition. Therefore, it was assumed that $200\ \mu\text{m}$ PTHs would be plated under a macroprofile or conformal boundary layer condition and the $100\ \mu\text{m}$ microvias would be plated under a microprofile or non-conformal condition. As such, based on the discussion above, it would be surprising if similar waveform parameters would be applicable to the different sized features under both macroprofile and microprofile boundary layer conditions.

In essence, plating a z-axis interconnect is similar to plating around a corner. Inhibition of plating at the high current density corner was the reason for the development of plating additives for DC plating. The additives block deposition on the high current density regions, essentially leveling the deposit. However, when using PRC plating, since copper is approximately 100% current efficient for both the cathodic deposition of copper and anodic dissolution of copper, the problem may be thought of as designing the cathodic pulse to minimize the copper over-plating at the corner, and as designing the anodic pulse to accentuate copper dissolution at the corner that had over-plated during the preceding cathodic pulse. In this manner the net effect would be a conformal coating around the corner.

By combining this strategy with a conceptual understanding of the influence of a macroprofile (a PTH) or microprofile (a microvia) on the effect of an applied current pulse on current distribution, it seemed possible that conformal plating of PTHs and microvias could be done in a single process step using a sequence of two waveforms: a generalized “macroprofile waveform” (Fig. 8a) and “microprofile waveform” (Fig. 8b), respectively. While these concepts do not provide precise waveform parameters, they did provide general guidance for examination of the PRC waveform parameter space for plating the z-axis interconnects for electronic applications.

Per the discussion summarized in Fig. 6, the macroprofile waveform for the PTHs was designed as a relatively long on-time, low current cathodic pulse resulting in slightly more non-uniform deposition (compared to DC) around the corner by focusing on mass transport control, followed by a relatively short on-time, high current

anodic pulse to provide significantly more non-uniform removal of copper from the corner by deemphasizing mass transport control and preferentially focusing on primary and secondary current distribution. The net effect was good throwing power at high rates for PTHs.

Conversely, the microprofile waveform for the microvias was designed as a relatively short on-time, high current cathodic pulse to achieve significantly more uniform deposition around the corner by converting the microprofile to a macroprofile by establishing a small δ_p via a small t_c (see Eqn. (5)), and maintaining large component of tertiary current distribution control by establishing a relatively small τ , so that $(t_{\text{cathodic}}/\tau) \gg 1$. This was accomplished by using a large I_{cathodic} (see Eqn. (6)). This was followed by a relatively long on-time, low current anodic pulse to provide non-uniform removal of copper from the corner by maintaining the microprofile and mass transport control. I_{cathodic} was low, so to maintain $(t_{\text{cathodic}}/\tau) \gg 1$, t_{cathodic} had to be long. The net effect was good throwing power at high rates for microvias.

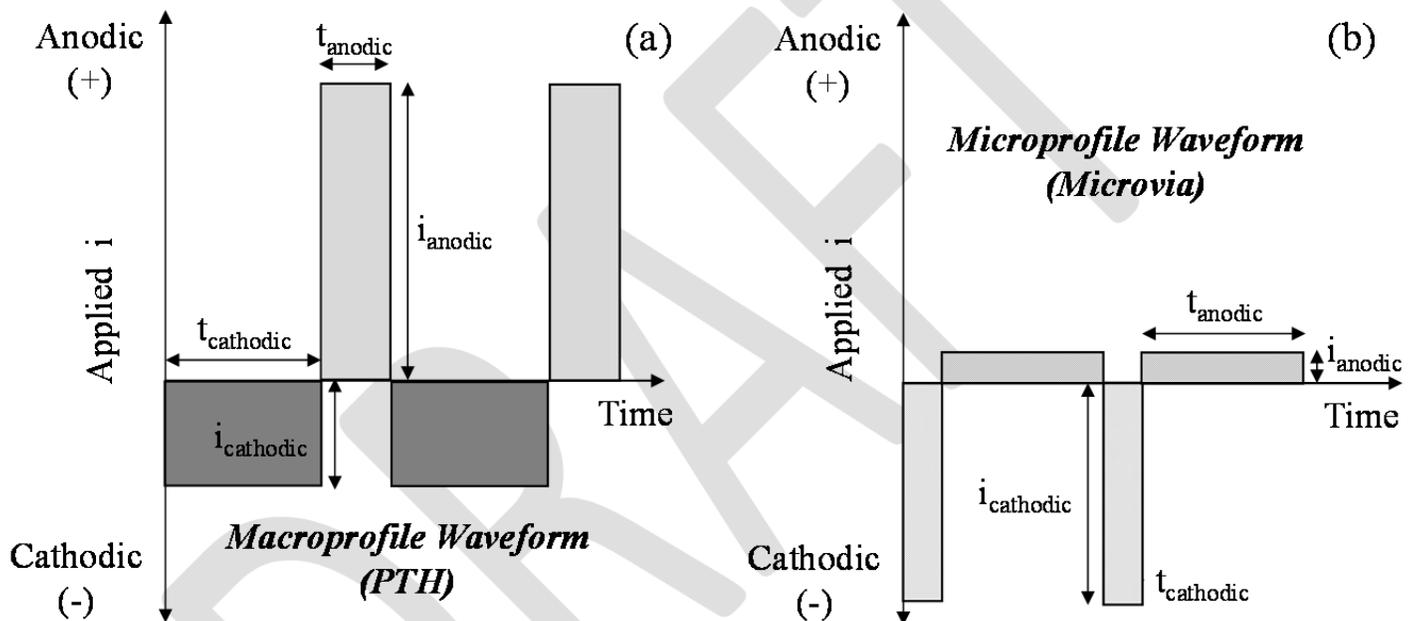


Fig. 8. Illustration of (a) macroprofile waveform and (b) microprofile waveform.

From the previous work with the chemical formulator, the macroprofile waveform had been validated for plating 325 μm PTHs under macroprofile boundary layer conditions in the absence of leveling additives. To test the microprofile waveform concept under microprofile boundary layer conditions, copper plating experiments were conducted in a bath without leveling additives on brass substrates into which 100 μm holes had been mechanically drilled [34,35,36,37]. In all cases, the average current was 35 mA/cm^2 . In Figs. 9a-f the results of these experiments are summarized. In Fig. 9a is a cross section for DC plating. As expected, a “key-hole” is formed due to preferential plating at the high current density corner. Fig. 9b is a cross section for PC plating. Again, severe voiding is evident in the cross section. Fig. 9c is a cross section for PRC plating with the macroprofile waveform. Under these conditions the copper deposit essentially “bridges” across the opening of the feature and exhibits a worse condition than the DC plating. A PCB process engineer observed this data at a tradeshow and verified that this is what happens when their leveling additive is out of specification. Essentially, they were correcting a worse current distribution than DC with bath additives! Fig. 9d is a cross section for PC

plating at a higher frequency. The higher frequency appears to improve the plating of the feature and does employ a short cathodic on-time similar to the microprofile waveform. However, the situation is still unacceptable. Fig. 9e is a cross section for PRC plating with the microprofile waveform. The desired conformal coating is observed. Finally, continued plating with the microprofile waveform leads to filling of the feature with a level overplate as evident in Fig. 9f. The flexibility inherent in the process enables cases where conformal coating of small features is desired as well as other cases featuring filling is desired.

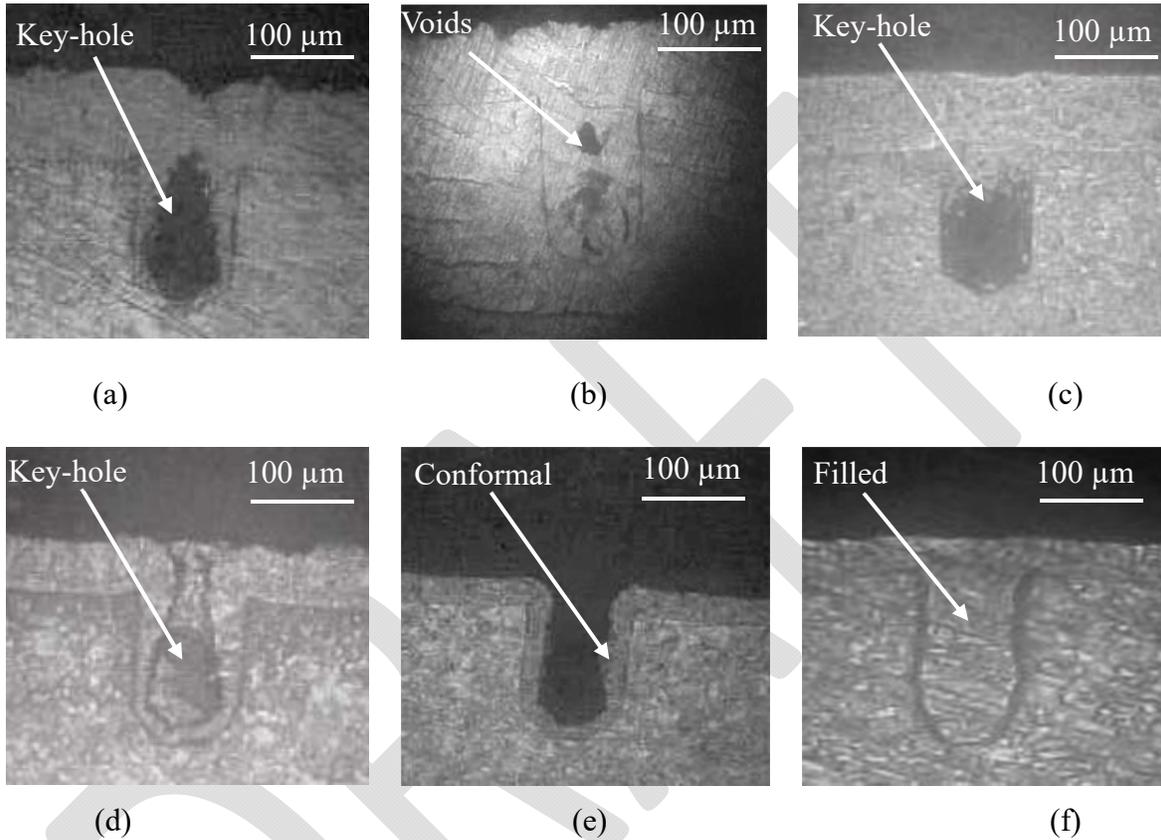


Fig. 9. Plating of a 100 μm feature under microprofile boundary layer conditions from a copper bath without brightener (a) DC plating, (b) PC plating, (c) PRC plating with a macroprofile waveform, (d) PRC plating with the macroprofile waveform at higher frequency, (e) PRC plating with a microprofile waveform, (f) PRC plating with the microprofile waveform for a longer period of time.

Using the macroprofile waveform approach, the ability to copper plate PTHs with high aspect ratios was demonstrated [38]. Using the microprofile waveform approach, the ability to copper fill features as small as 0.25 μm without additives was demonstrated [39]. In addition, the ability to plate multiple feature sizes representing PTHs and microvias was demonstrated, on the same board, in the same process step, using a sequence consisting of the macroprofile waveform followed by the microprofile waveform [40,41,42,43]. While these activities demonstrated the utility of pulse reverse current plating for controlling current distribution, at technical conferences chemical formulators would still question the ability of pulse reverse current plating of copper to deliver good mechanical properties from plating bath chemistries that did not contain additives.

3.2 Ductility without Brighteners using Pulse Current Plating

Copper-plated z-axis interconnects for PCB applications need to exhibit sufficient ductility in order to sustain the thermal shock of soldering operations without cracking. In conventional DC plating, chemical formulators provide additives, such as “brighteners”, to ensure that the plated copper exhibits sufficient ductility to avoid cracking. The ductility of the copper deposits is understood to result from small grained copper deposits. As noted above, high pulse current at short on-times would be expected to favor nucleation vis-à-vis growth, and consequently result in fine grained deposits.

A PCB manufacturer funded work to prepare standard tensile samples using pulse reverse current plating from a copper plating bath devoid of brighteners [44]. The mechanical properties of the PRC-plated tensile strips were compared to the mechanical properties of tensile strips plated under DC conditions in the conventional additive chemistry of the PCB manufacturer. Both tensile test strips were plated at an average current density of 25 mA/cm². The stress versus elongation data for the DC and PRC plated tensile strips are presented in Figs. 10a and 10b, respectively. Both samples passed the Institute for Printed Circuits specification of an ultimate tensile strength of at least 36,000 psi and an elongation of at least 12%. Interestingly, the stress elongation curves for the PRC-plated samples exhibited a lower standard deviation. More studies would be required to establish that the enhanced reproducibility of the PRC samples is real. However, these observations demonstrated that PRC-plated copper could yield acceptable mechanical properties without the addition of brighteners to the plating bath.

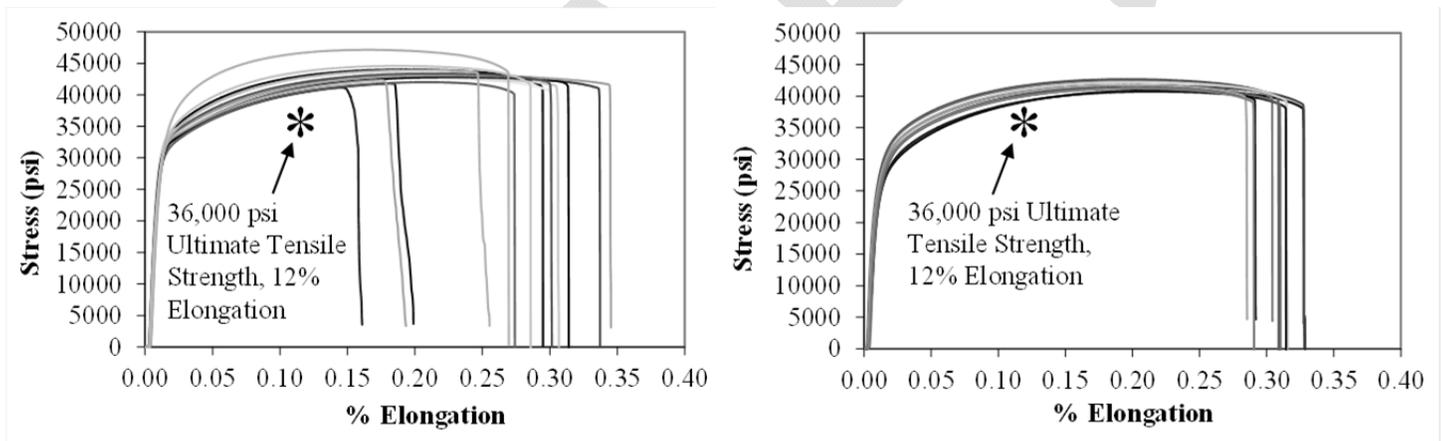


Fig. 10. Stress-strain data for copper tensile specimens plated with (a) DC from a bath containing brighteners, (b) PRC from a bath without brighteners.

In summary, the combination of cathodic and anodic pulses can be net cathodic or net anodic. The principles outlined above apply equally to both cases, in terms of the effect on the balance of primary, secondary and tertiary current distribution. However, the effect of that current on the surface state and electrochemical reactions may range from very simple to very complex. It is perhaps serendipitous that this journey began in the copper plating system, as copper deposition is a simple, 100% current efficient and reversible process. It was relatively easier to develop the preliminary guidelines that allowed the manipulation of the pulse reverse parameters to obtain the desired result in a system where there are little or no side reactions, and what is readily deposited may be readily removed. Other systems, such as electropolishing of strongly passive materials, are more complex and the current response to a voltage pulse may be more difficult to interpret.

4 Transition of Pulse Current Plating Concepts to Surface Finishing

Within a few years of founding, Faraday was beginning to establish a reputation in the field of electrochemical research, development, and engineering. Specifically, an approach to electrochemical process engineering was being developed that challenged the conventional paradigm of DC processing with additive chemistry control. In addition to being approached by companies interested in solving plating problems, the company was also approached by companies with surface finishing challenges, such as electrochemical deburring and electrochemical polishing. Historically, like electroplating, conventional electrochemical surface finishing has also been based on the chemical control paradigm. As will be discussed below, a similar paradigm shift was observed in this technology area, by manipulation of electric field parameters to reduce or eliminate difficult-to-control and/or toxic chemistries, while maintaining or improving performance based metrics.

4.1 Pulse Voltage Deburring of Automotive Planetary Gears

Removing rough edges and burrs from manufactured parts is an important industrial challenge. Deburring is often accomplished with manual labor using rudimentary tools and implements, resulting in issues in terms of cost, quality, and worker repetitive motion injury. In the mid-1990s, the company was approached by a machine builder who had been contracted to install an electrochemical deburring process for planetary gears at Ford Motor Co.'s Power Train Division in Livonia, Michigan. Ford manufacturing engineers sought a reproducible cost-competitive process to replace their current manual deburring activities. The part of interest was a cast iron (SAE 1010 steel) planetary carrier with oil grooves that had rollover burrs from the milling process. Initially, Ford engineers worked on an electrochemical deburring process based on an electrolyte primarily consisting of ethylene glycol with additions of ammonium salts and a small amount of water [45]. The process had been successfully employed for a number of electrochemical surface finishing problems, generally at limited volume batch level processing. Ford's initial bench scale experiments indicated that the planetary gears could be deburred in ~45 seconds or less.

The electrochemical dissolution of relatively large features (arbitrarily defined as $>1 \mu\text{m}$) is termed anodic leveling or macrosmoothing while the removal of relatively small features (arbitrarily defined as $<1 \mu\text{m}$) is defined as anodic brightening or microsmoothing [46]. The deburring of Ford planetary gears falls into the category of macrosmoothing. For macrosmoothing using a DC process, the current is focused on the burr by altering the primary current distribution by the use of a highly resistive electrolyte, such as ethylene glycol. This adheres to the conventional electrochemical engineering paradigm of chemical process control under a DC field. As shown schematically in Fig. 11, by using the highly resistive electrolyte, the burr is preferentially dissolved relative to the surface of the gear via the generalized reaction:



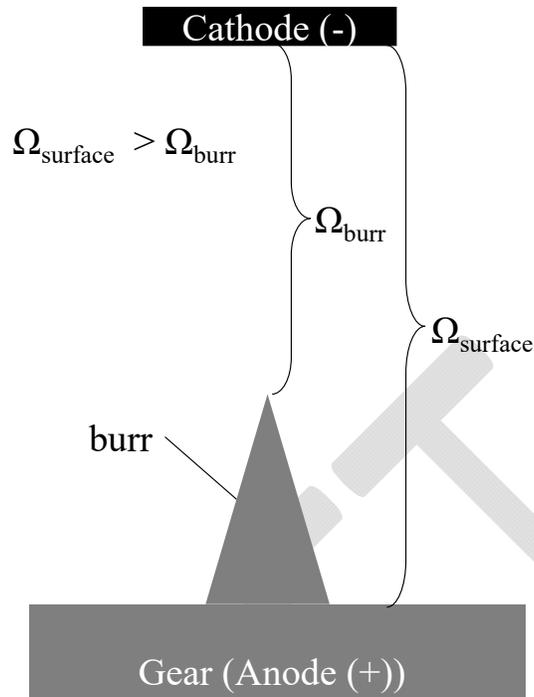


Fig. 11. Schematic illustration of electrochemical deburring with a highly resistive electrolyte.

The Ford application required a throughput of ~ 400 parts per hour. To accomplish this high volume throughput, the machine tool maker constructed a sixteen-station automated programmable logic controller (PLC) machine. Eight stations were electrochemically deburring planetary gears while the other eight stations were unloading processed planetary gears and loading planetary gears to be processed. During initial production trials, the electrolyte heated up due to the large amount of current being passed through the highly resistive ethylene glycol electrolyte and thermal runaway occurred within about 30 minutes. Even with active chilling of the electrolyte, several problems were noted, specifically, 1) a noticeable ammonia odor, 2) limited tool (cathode) lifetime, and 3) the electrolyte was difficult to maintain and expensive to replace.

Engineers from Ford and the machine tool maker funded work to investigate whether their electrochemical deburring process could be modified to meet the ~ 400 parts per hour designed throughput. From a current distribution perspective, electrochemical deburring is simply bump plating in reverse. Applying the principles determined in copper plating, it was speculated that by using pulse currents (voltages) instead of DC the Ford planetary gears could be effectively deburred in a simpler non-resistive electrolyte. Note, while surface finishing is generally conducted under voltage control, the waveform is generally referred to as pulse current (PC) or pulse reverse current (PRC) surface finishing similar to the use of DC surface finishing.

The same benchtop apparatus and cathode tooling as that used by the Ford engineers for the ethylene glycol-based process was used to study pulse current deburring. The planetary gear was fabricated from SAE 1010 steel and after some initial trials, a $\sim 12\%$ (w/w) NaCl aqueous solution was identified as the ideal electrolyte. Several experimental trials in the benchtop apparatus indicated that pulse current waveforms of $\sim 25\%$ duty cycle could effectively remove the burrs within the established part dwell time of < 45 sec [47,48]. A picture of the planetary gear and cathode tool as well as an oil groove before and after deburring is shown in Fig. 12. The process was transitioned to the fully automated production machine where a 5000-part production run-off with

zero failures was completed. The process has been in full production at Ford Power Train Division since early 1996 [49]. Ford has reported that the “saltwater” electrolyte costs a fraction of the cost of the proprietary ethylene glycol electrolyte and electrolyte maintenance is simple. Specifically, water is added twice monthly to replace the water lost by evaporation and the electrolyte is replaced about every six months primarily to avoid adverse effects associated with oil drag-in. Thus, the paradigm of DC deburring in a highly resistive electrolyte was changed to PC deburring in a simple, conductive electrolyte.

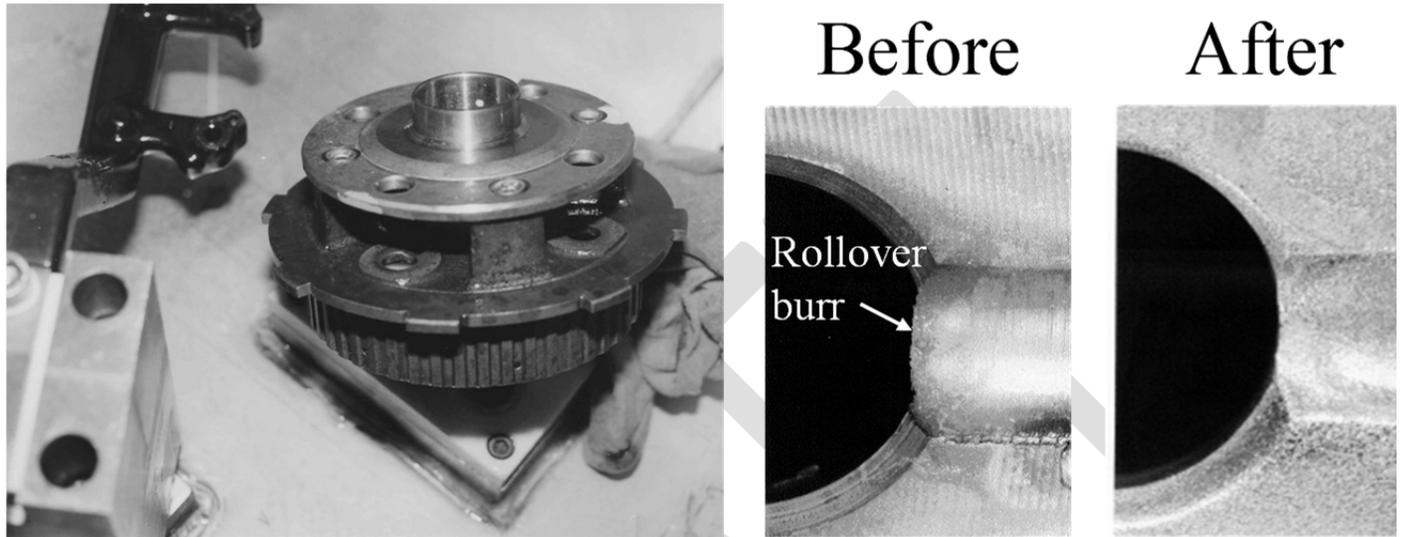


Fig. 12. Picture of (a) planetary gear and cathode tool and (b) oil-groove before and after deburring.

4.2 Transition to Pulse Reverse Voltage Electropolishing of Passive Materials

The successful development and implementation of a pulse current (voltage) process for deburring of automotive planetary gears opened up another set of applications and the company vision was expanding from PC/PRC plating processes to PC/PRC surface finishing processes, such as leveling (macrosmoothing) and brightening (microsmoothing) of metal surfaces by electrochemical anodic dissolution. In addition to deburring, electrochemical machining, electrochemical through-mask etching, and electropolishing are an industrially important surface finishing applications [4]. The Jacquet paradigm established that electropolishing, as opposed to electrochemical etching (or pitting as originally described by Jacquet), is accomplished by polarizing the DC voltage in the mass transport region of the polarization curve illustrated in Fig. 13. With time, a viscous salt film builds up in the valleys and the asperities are removed under mass transport control. The nature of the mass transport controlled species is generally speculated to be either the dissolving metal ion or an “acceptor” species [50]. The mass transport limited dissolving metal ion through a viscous salt film generally occurs in high water content electrolytes such as those used in electrochemical machining. The mass transport limited acceptor species generally occurs in low water content electrolytes, such as viscous concentrated phosphoric and sulfuric acids used in electropolishing. The acceptor species can be water itself. A number of studies attempt to elucidate the mechanistic details of the mass transport-limited process, such as mass transport limited metal ion diffusion through a viscous salt film [51], mass transport-limited acceptor species [52], and mass transport-limited water acceptor species [53,54]. Regardless of the exact mechanism, it is widely accepted that mass transport plays an important role in surface finishing in general and electropolishing in particular as schematically illustrated in Fig. 14.

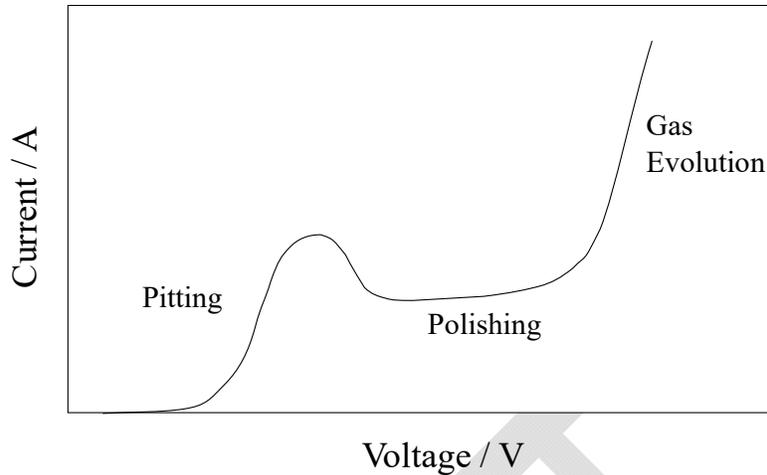


Fig. 13. Schematic illustration of the region of the polarization curve purported by Jacquet to enable electropolishing [4].

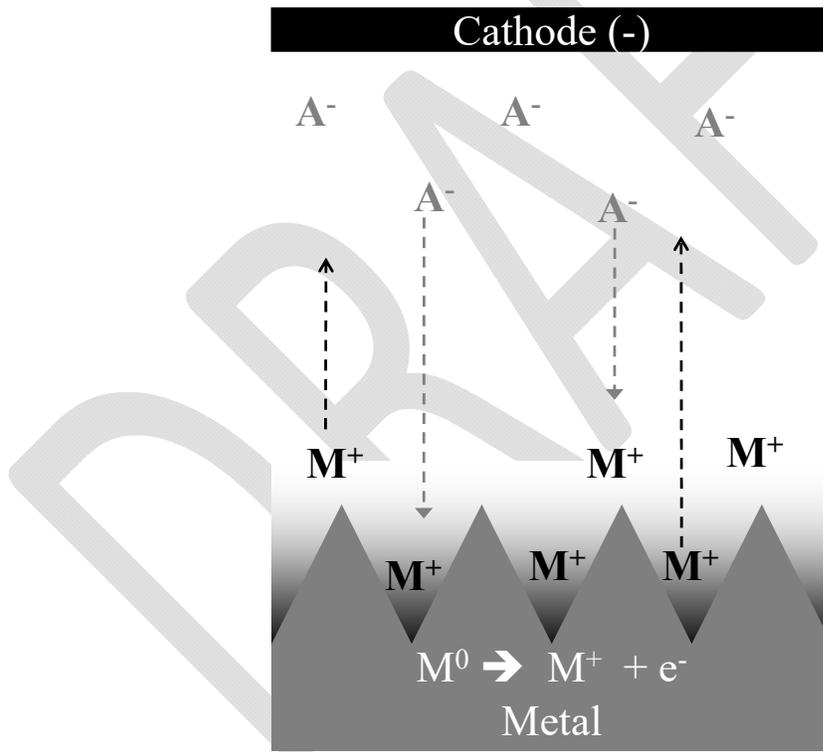


Fig. 14. Schematic illustration of the Jacquet paradigm of mass transport

With the success of PC deburring of automotive planetary gears, SBIR funding from the National Science Foundation and US Air Force SBIR programs was obtained to develop surface finishing processes for materials of commercial and Department of Defense military interest. These materials included stainless steel, nickel alloys and titanium alloys. During electrochemical anodic dissolution, these materials would develop a passive oxide layer via the competing anodic reaction, generally described as:



The conventional DC electropolishing paradigm to mitigating the adverse effect of the oxide layer formation during electropolishing involves either 1) concentrated acid solutions, such as mixtures of sulfuric and phosphoric acid, to chemically remove the oxide layer for mildly passive materials such as stainless steels [55, 56, 57], 2) addition of fluoride salts or hydrofluoric acid to chemically remove the oxide layer for strongly passive materials such as niobium, nickel-based and titanium-based alloys [58], or 3) use of low water content or non-aqueous ionic liquid solutions to avoid or minimize oxide formation for strongly passive materials [59,60].

Initial work focused on electropolishing of INCONEL[®],¹ alloy 718 coupons in simple aqueous solutions, such as the salt water electrolyte developed for the automotive gear, using anodic only pulse currents (PC). However, the use of a PC waveform resulted in a rougher surface [61], attributed to localized breakdown of the oxide film, analogous to pitting corrosion.

Prior observations with pulse reverse current (PRC) plating were applied to address the issue of oxide layer formation during anodic dissolution in aqueous electrolytes without the use of concentrated acids and/or addition of fluoride species. At about this stage of finishing process development, funding was awarded from the Environmental Protection Agency SBIR program to replace chromium plating from hexavalent chrome plating baths with an environmentally and worker friendly trivalent chrome plating bath. While decorative chromium coatings were plated from trivalent chrome plating baths, functional chromium coatings were only plated from hexavalent plating baths. As reported in the literature, chromium coatings from a trivalent chrome plating bath were limited to thicknesses that were not sufficient for functional applications requiring properties such as high hardness and wear resistance. The faradaic efficiency for chromium plating from trivalent chrome plating baths was quite low, with ~15% of the current attributed to the desired chromium plating reaction (13) and ~85% of the current attributed to the hydrogen evolution reaction (14):

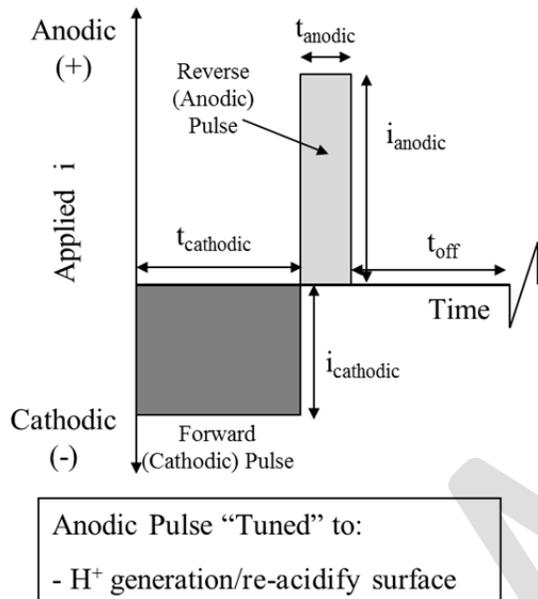
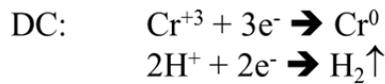


Generally, after plating of less than ~2.5 μm , the chromium plating ceased. The generation of hydrogen due to the low faradaic efficiency could have resulted in an alkaline pH at the interface leading to a species which adversely affected the continued plating of the chromium [62]. Consequently, there was speculation that insertion of an anodic reverse current pulse during pulse current plating could “re-acidify” the interface and allow plating to continue. Using pulse reverse current plating, the ability to plate thick chromium coatings from a trivalent chrome plating bath was successfully demonstrated [63].

In the case of surface finishing of passive or oxide forming materials, there is an analogous adverse reaction (12) of oxide formation. Therefore, it was speculated that the adverse effects of the oxide formation reaction during surface finishing could similarly be eliminated by inserting a cathodic reverse current pulse during pulse current surface finishing to remove the oxide layer formed during the anodic forward pulse. The parallels between eliminating the adverse effects of hydrogen evolution during plating and eliminating the adverse effects of oxide layer formation during surface finishing are illustrated in Figs. 15a and 15b, respectively. While the exact mechanisms of these two approaches have not yet be fully elucidated, this approach was used by analogy to successfully demonstrate pulse reverse current electropolishing of stainless steels, nickel alloys and titanium alloys in aqueous sodium chloride/sodium nitrate salt electrolyte [64,65].

¹ INCONEL is a registered trademark of the Special Metals group of companies.

Plating of Low Faraday Efficiency Deposits



Surface Finishing of Passive Materials

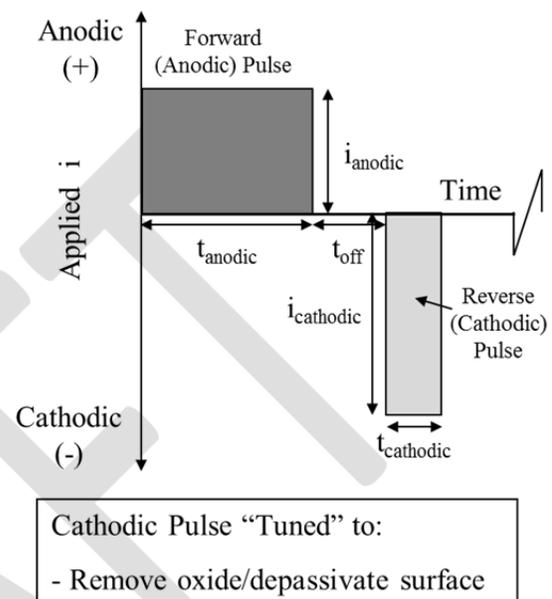
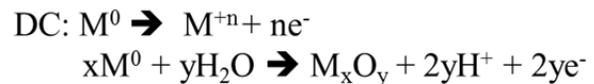


Fig. 15. Schematic illustration of PRC approaches to mitigate (a) adverse effect of hydrogen evolution during plating and (b) adverse effect of oxide layer formation during surface finishing.

4.3 Sequenced Pulse Reverse Voltage Electropolishing of Semiconductor Valves

Soon after presenting and publishing the pulse reverse voltage electropolishing results for passive materials, the company was approached by a manufacturing engineer from Swagelok Corporation. Swagelok was using conventional direct voltage electropolishing as the final surface finishing step for their stainless (300 series) steel valves, fittings and tubular products. These were specialty products for the semiconductor and biomedical industries, and the internal surfaces of these valves required a mirror-like finish. Due to the slow material removal rate of conventional electropolishing (viscous electrolytes operating under mass transport control), Swagelok used a two-step surface finishing process, 1) abrasive flow machining (AFM) for deburring and bulk material removal of tool lines, followed by 2) conventional electropolishing to achieve the final mirror-like surface finish. The electropolishing process used a chilled electrolyte solution consisting of concentrated sulfuric/phosphoric acid as well as proprietary additives that may have included fluoride species. The electropolishing process required ~160 seconds to achieve the final mirror-like finish. The AFM media was expensive and the combined AFM/electropolishing process was difficult to control.

Under a stage-gated research-for-hire activity funded by Swagelok, electropolishing of stainless steel coupons of their specific 300 series valves in an aqueous solution of ~12% NaCl/NaNO₃ salt electrolyte without addition of fluorides was demonstrated. The next stage-gate involved transitioning the process to actual production hardware and actual products. The focus was to replace both the AFM and electropolishing process steps with a

single surface finishing process based on pulse reverse voltage in a simpler electrolyte. Swagelok moved one of their electropolishing manufacturing cells (Fig. 16) with a representative valve to the company's α -scale prototyping area. Swagelok's concentrated acid electropolishing electrolyte was switched out with the simpler aqueous salt solution and replaced their DC rectifier with a PRC rectifier. Initial experimental electropolishing trials indicated that the pulse reverse voltage waveforms could remove the burrs and reduce the Ra from $\sim 1 \mu\text{m}$ to $\sim 0.2 \mu\text{m}$ within about 30 secs. Continued electropolishing up to about 2.5 minutes resulted in no improvement in the Ra and the surface exhibited an "orange-peel" structure indicative of electrochemical etching in lieu of electropolishing.

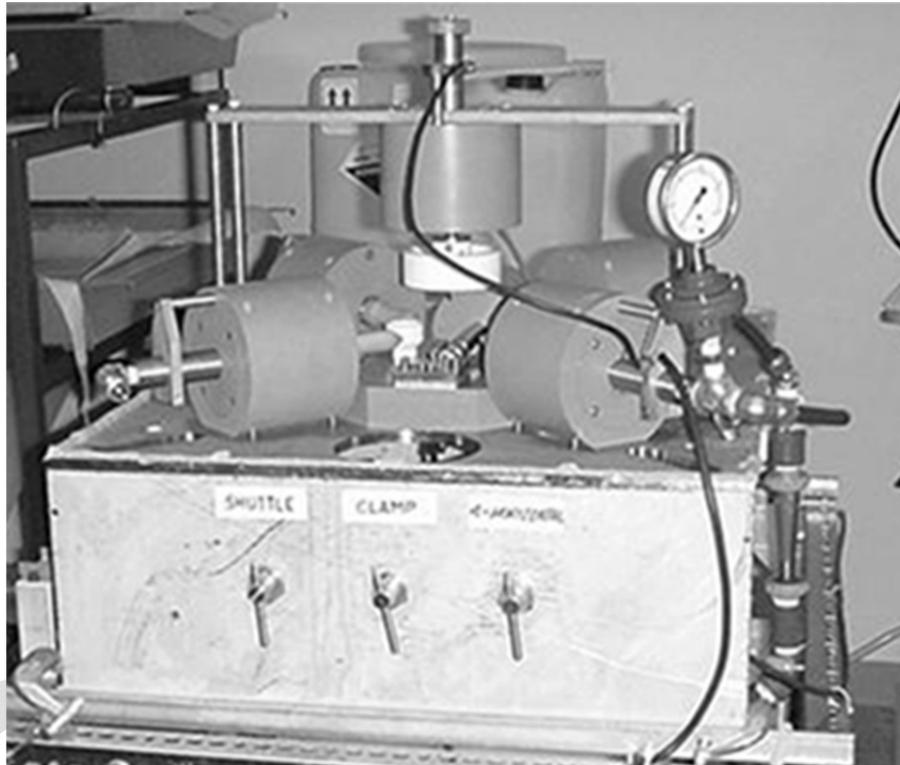


Fig. 16. Swagelok α -scale manufacturing cell on location.

To better understand this transition from surface smoothing to etching, previous theoretical and experimental studies by Landolt and collaborators were considered that examined anodic dissolution of well-defined triangular surface profiles under DC conditions [66,67]. The geometrical setup considered both experimentally and theoretically is depicted in Fig. 17 where "L" is the gap between the surface and the electrode, " β " is the angle of the model surface asperity, and "l" is the amplitude of the surface asperity.

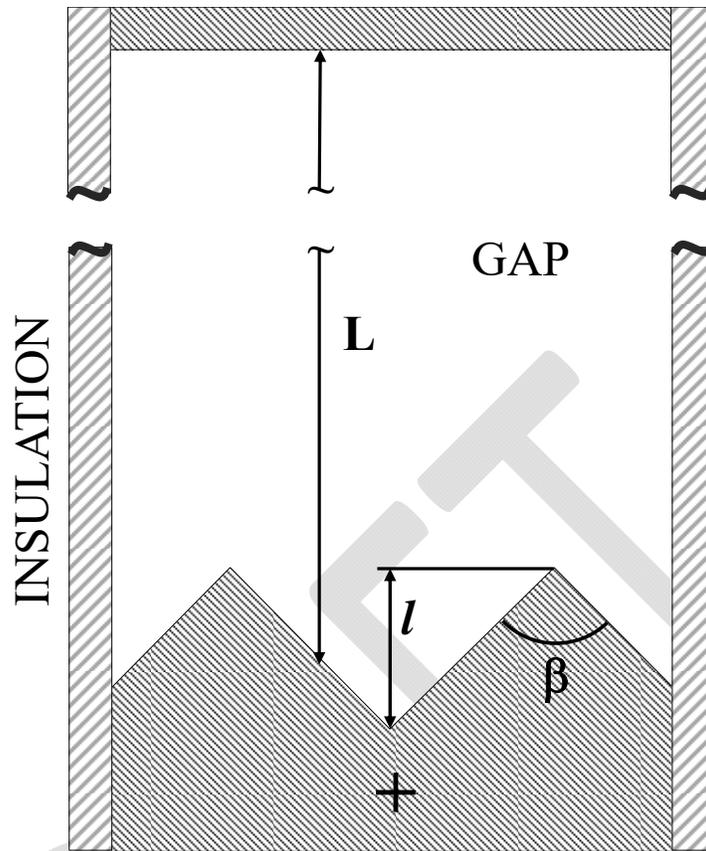


Fig. 17. Model geometry used for theoretical and experimental studies of DC electropolishing.

The experimental and modeling studies maintained $L \gg l$, and l was considered the characteristic length in the Wagner number (see Eqn. (9)). The parameters “ β ” and “ l ” represent the surface roughness and as electropolishing progresses “ β ” to increase and “ l ” were expected to decrease. As “ l ” decreases the Wagner number increases, the current distribution becomes more uniform. Landolt and collaborators experimentally verified that as “ l ” decreased and “ β ” increased the effectiveness of the electropolishing process decreased.

As noted above, the same behavior was observed when electropolishing the Swagelok valves. Initially, the surface roughness was reduced, i.e. “ l ” decreased, but after 30 seconds of processing, the surface roughness stopped improving. Since “ l ” decreased, the Wagner number increased, resulting in a shift towards more secondary current distribution, and therefore a more uniform material removal rate at the peaks and valleys of the asperities. To continue to improve the surface finish, the balance of primary, secondary and tertiary current distribution needed adjustment back towards primary control. Using DC processing, this would only have been possible by changing the tool geometry and/or solution conductivity. However, in the spot plating of gold example described earlier, Chin et al. [24] showed that pulsed processing could decrease the Tafel slope and therefore the Wagner number towards zero, making it less uniform. In other words, pulsed processing gives us another tool to manipulate the current distribution to achieve more or less uniformity as required, with consideration of the impact of macroprofile or microprofile.

Although the prior work was under conventional DC “leveling” conditions, it was assumed that similar phenomena were impacting the ability to electropolish the Swagelok valves. It was noted that the manufacturing apparatus did not submerge the complete valve into the electrolyte but rather “jetted” the polishing solution into

the internal diameter of the valve body. Initially the boundary layer resulting from the high flow velocity represented a macroprofile boundary layer during the initial stages of electropolishing. After ~30 sec of electropolishing, the speculation was that the surface roughness was sufficiently smoothed, whereby the boundary layer became a microprofile. At this point, the “macroprofile waveform” induced uniform electropolishing of the peaks and valleys of the asperities, rather than peaks only.

The waveform was changed per the design guidelines described in Fig. 6 so as to induce significantly more non-uniform polishing under a microprofile condition, to continue the reduction in surface roughness. Consequently, after 30 sec of electropolishing the pulse reverse voltage waveform was sequenced from short-anodic/long-cathodic pulses to long-anodic/short-cathodic pulses for an additional 15 sec. As illustrated in Fig. 18 [68], using the sequenced waveform parameters, the surface Ra was further reduced from 0.2 μm to 0.026 μm with a mirror-like finish and complete absence of the “orange-peel” structure (Fig. 19). Consequently, the pulse reverse voltage approach replaced both the AFM and the conventional DC electropolishing steps and

- 1) Enabled a simpler aqueous electrolyte without the need for concentrated, viscous, or chilled acids with the addition of fluorides,
- 2) Required ~45 sec compared to the ~160 sec required for conventional electropolishing step alone,
- 3) Lead to a more robust process, and
- 4) Replaced an expensive consumable.

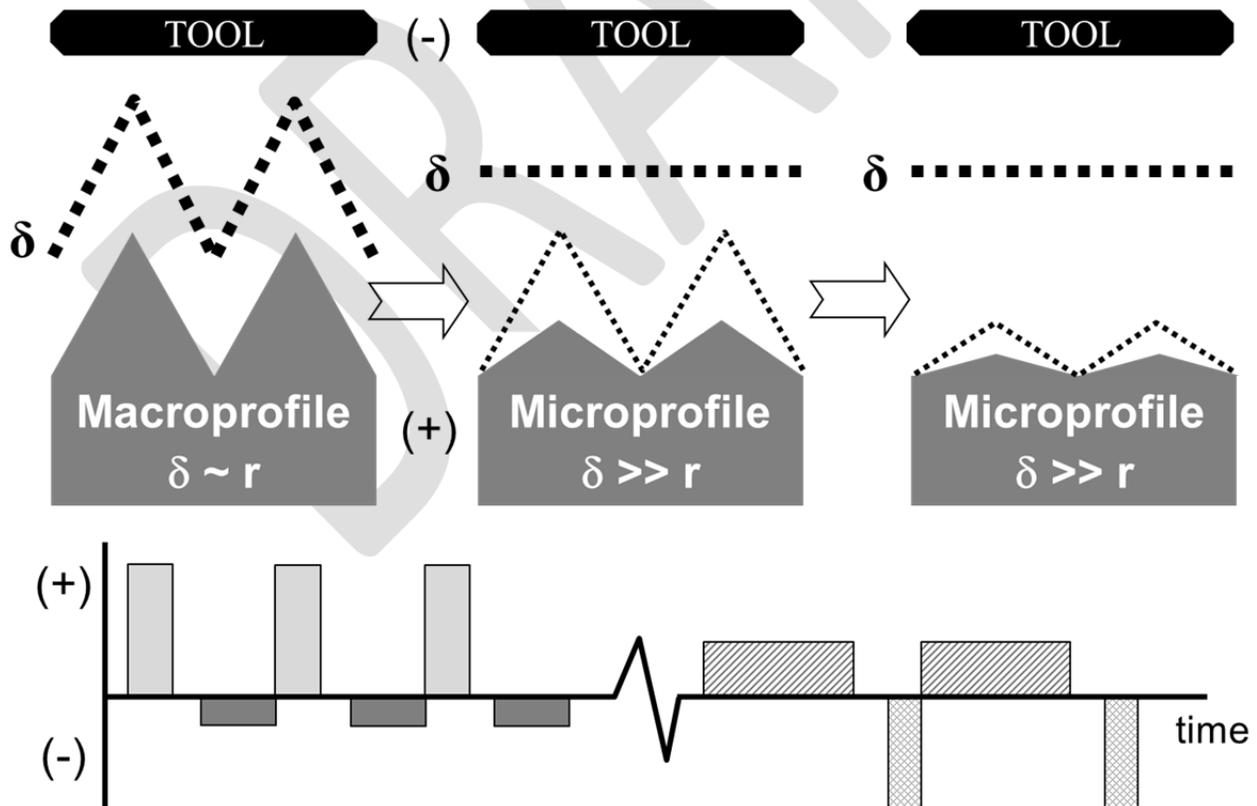


Fig. 18. Schematic representation of the sequenced waveform used to electropolish the stainless valves.

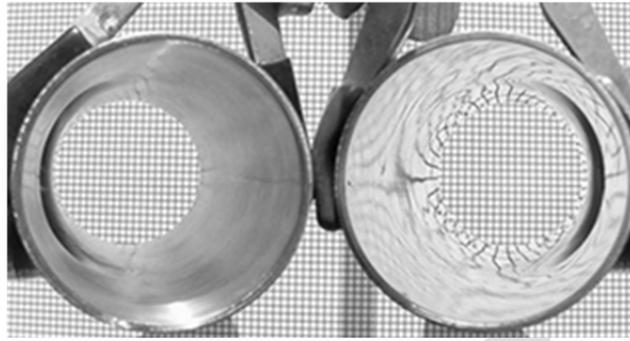


Fig. 19. Sample part before (left) and after (right) electropolishing in an aqueous salt solution.

In summary, the similar reasoning that lead to the macroprofile and microprofile waveforms for plating various size electronic z-axis interconnects lead to an analogous approach to surface finishing. The pulse reverse voltage electropolishing process using the low viscosity aqueous salt electrolyte has been in production by Swagelok Corporation since 2000 [48].

4.4 Pulse Reverse Voltage Electropolishing of Strongly Passive Materials

The successful demonstration of pulse reverse voltage surface finishing of stainless steel, nickel and titanium based alloys as well as the implementation of PRC surface finishing of Swagelok valves opened the door for numerous applications for surface finishing of these and other materials. In the mid-2000s, an SBIR project from the Department of Energy (DOE) was awarded to apply the pulse reverse current approach to electropolishing of niobium. Niobium is a superconducting metal and is used to fabricate superconducting radio frequency (SRF) cavities for particle accelerators, such as the International Linear Collider, as well as other high energy physics projects. Maximizing the particle accelerating electric fields in these SRF cavities requires eliminating or minimizing surface defects on the interior surface of the cavities.

For more than thirty years, electrochemical surface finishing or electropolishing has been the fundamental surface preparation process to achieve high gradients and quality factors for current and proposed SRF-based accelerators using elliptical cavities. The benefits of electropolishing niobium cavities are well known to the SRF community [69,70]. Electropolishing of SRF cavities is based on the well-established “viscous salt film” model by Jacquet [4], and utilizes a viscous electrolyte consisting of a mixture of sulfuric acid (95-98%) and hydrofluoric acid (49%) in an approximately 9:1 volume ratio [71].

Jacquet’s initial research was directed toward the electropolishing of copper and his “viscous salt film model” fits the definition of a paradigm. The Jacquet paradigm was open-ended and provided a framework for subsequent researchers to develop electropolishing processes for other metals and alloys. These subsequent studies enhanced the Jacquet paradigm by clarifying the nature of the mass transport limited species for specific material and electrolyte systems. Consistent with the Jacquet paradigm [4], the concentrated sulfuric acid establishes a thick boundary layer that leads to surface smoothing when a direct anodic current is applied such that the niobium dissolution operates under mass transport control. The concentrated hydrofluoric acid function is to form a soluble species with the dissolved niobium and to remove the oxide film formed during niobium dissolution [58,72]. A mechanistic study reported by a research team including the DOE Thomas Jefferson National Accelerator Facility definitively demonstrated that state-of-the-art electropolishing of niobium occurs

by diffusion-limited transport of fluoride ions to a compact salt film [71]. This finding is consistent with other studies generally indicating that an acceptor ion is the mass transport limited species for low water content electrolytes. Due to the slow material removal rate of electropolishing, SRF cavity surface finishing utilizes a two-step surface finishing process similar to Swagelok. The first step is “buffered chemical polishing” (1:1:2 HNO₃(69%):HF(49%):H₃PO₄(85%)) to remove ~ 100 μm of material to a Ra of ~1 μm. This is followed by an electropolishing step that removes ~ 30 μm of material to a Ra of < 0.2 μm, although the final surface finish is typically mirror-like.

Significant negative aspects are associated with niobium SRF cavity electropolishing as currently practiced [73]. Specifically, electropolishing with a mixture of concentrated sulfuric and hydrofluoric acids carries significant personnel safety risk, as well as negative environmental impact. Consequently, SRF cavity processors must abide by stringent regulations from both the Occupational Safety and Health Administration (OSHA) and the Environmental Protection Agency (EPA). In addition, the use of the concentrated hydrofluoric and sulfuric acid mixture significantly impacts both the capital and operating costs of cavity processing and is a barrier to establishing an industrially compatible cavity surface finishing process. Consequently, there has been a long-felt need for an environmentally friendly electropolishing process for niobium SRF cavities that is also compatible with industrial practice. The DOE SBIR topic call was directed towards an “eco-friendly” niobium SRF cavity electropolishing process.

While the pulse reverse current approach had previously been used to replace concentrated acid electropolishing electrolytes, including those with fluoride salt additions, this approach had not been used to replace electropolishing processes where concentrated hydrofluoric acid was directly added as a significant component of the electropolishing electrolyte. These materials generally exhibit <-600 kJ/mol free energy of oxide formation on the Ellingham diagram and in addition to niobium, include titanium, tantalum, tungsten and molybdenum. Within the DOE SBIR Phase I feasibility activity, the ability to electropolish niobium coupons to a mirror finish (Fig. 20) had been successfully demonstrated in aqueous solutions of sulfuric acid of 5 to 30% (w/w), without hydrofluoric acid! Atomic force microscope scans by Dr. Charles Reece of DOE Thomas Jefferson National Accelerator Facility of 2500, 100 and 4 μm² areas indicated Ra values ranging from 3.5 to 0.36 nm [74]. The surfaces were comparable to those obtained using the conventional process based on hydrofluoric acid.

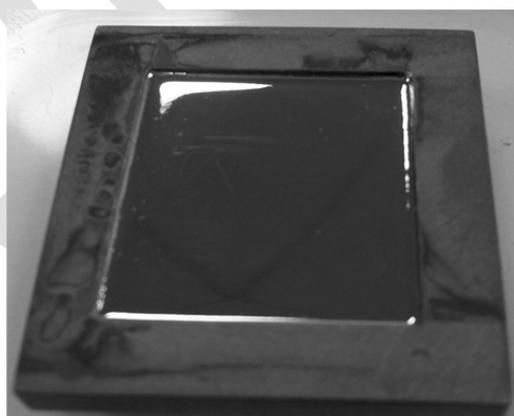


Fig. 20. Image of niobium coupon electropolished in 5% sulfuric acid by weight using pulse reverse voltage.

While the earlier work was highly successful, it was limited to flat niobium coupon surfaces of no greater than 1"x1" or an area of 6.25 cm^2. In contrast, a single cell SRF cavity has an internal surface area of $\sim 1230 \text{ cm}^2$ consisting of tubular and elliptical regions. Therefore, the logical next step was to submit a proposal directed towards gaining an understanding of how the pulse reverse voltage niobium electropolishing would scale to the larger surface areas and more complicated geometries of single cell cavities. A DOE Phase II proposal was submitted that would transition the coupon pulse reverse voltage parameters to internal tubes and curved half-cell hemispherical surfaces representative of the SRF single cell cavities.

About the same time, a request for proposal under the America Reinvestment in Research Act (ARRA) directed toward demonstration of an "eco-friendly" process for surface finishing of niobium SRF cavities was released from DOE Fermi National Accelerator Laboratory (FNAL). Discussions were held with the FNAL technical point of contact, Mr. Allan Rowe, who was very interested in the approach and encouraged submission of a proposal. The parameters of the ARRA solicitation did not permit extensive research and development activities, instead being directed towards validation of an eco-friendly process on single cell cavities using the existing electropolishing fixturing and apparatus. Ideally, the timing of the DOE Phase II SBIR and the ARRA programs would coincide and the SBIR program results would synergistically permit the research and development activities that could be applied to the ARRA single-cell SRF cavity validation.

The nature of the current review system is such that it must use experts in the scientific community who are familiar with the relevant paradigms in order to ensure scientific quality. When these experts are faced with data or observations that do not agree with the current paradigms, they may receive the new data with some skepticism. This seemed to be the case with the Phase II SBIR proposal, which was declined, based on the assumption that the demonstration of electropolishing of niobium coupons did not imply future success with full-size cavities. Since conventional electropolishing had originally been demonstrated on coupons and transitioned to SRF cavities and the new process was still, in fact, employing electropolishing, this seemed surprising. However, this skepticism was not limited to the review panels. A niobium coupon electropolished in aqueous sulfuric acid using pulse reverse voltage was shown to a well-respected electrochemical colleague who proclaimed

"...you can't do that..."

While initially perplexing, upon reflection it seemed that, in effect, this colleague could not "observe" the niobium electropolishing result because it did not fit the well-established Jacquet electropolishing paradigm.

4.5 Pulse Reverse Voltage Electropolishing of Niobium Superconducting Radio Frequency Cavities

While the DOE Phase II SBIR was not funded, the ARRA proposal did receive an award, and the effort was able to continue. As noted above, the ARRA program did not permit "extensive" research and development activities and required that an electropolishing apparatus be constructed similar to the one used in current SRF cavity electropolishing and placed in a cleanroom environment [75]. The idea was that their hazardous electrolyte and DC power supply would simply be replaced with the eco-friendly electrolyte and pulse reverse rectifier, analogous to the Swagelok activity. During the initial part of the ARRA program, work continued on pulse reverse voltage waveform development on flat niobium coupons up to 3"x3" ($\sim 60 \text{ cm}^2$) in scale. While this was a long way from the internal surface area of a single cell SRF cavity (1800 cm^2) and even further removed from the internal surface area of the nine-cell SRF cavities used in actual particle accelerators, these

experiments were used to transition the pulse reverse voltage electropolishing process from “coupons to cavities.”

The DOE Phase I SBIR approach used high voltage and high frequency waveform parameters. However, due to the high surface areas inherent in the single-cell and nine-cell SRF cavities, pulse on-times and peak voltages were limited at the scale for processing single-cell and nine-cell SRF cavities by the technical constraints of commercially available pulse reverse rectifiers.

During the investigation of pulse reverse waveforms for electropolishing of 1”x1” niobium coupons, effective polishing occurred when a current transition was observed in the anodic current response as shown in Fig. 21 [76]. The speculation was that during the first part of the anodic voltage pulse a niobium oxide film is formed on the niobium surface. After the “complete” formation of the niobium oxide film, oxygen evolution occurs during the remainder of the anodic voltage pulse. The shift from oxide formation to oxygen evolution could account for the observed anodic current transition. Further speculation suggested that the niobium oxide film is subsequently removed during the cathodic voltage pulse. This mechanism was termed “cathodic electropolishing.” A similar anodic current transition has been observed for other strongly passive materials such as tantalum and nickel-titanium shape memory alloys. Synergistically, in parallel to the niobium electropolishing activities, funding was awarded from the National Institutes of Health (NIH) SBIR program directed towards electropolishing of nickel-titanium materials for medical shape set devices, such as stents. This work has led to successful development and licensing of a PRC process for electropolishing of nickel-titanium wire.

Note, the applied waveform in Fig. 21 appears to be net cathodic. However, it can be assumed that both the anodic and cathodic pulses are not 100% current efficient and water electrolysis reactions are taking place. While additional studies and optimization are required to elucidate the contributions of the water electrolysis during the anodic and cathodic pulses, material is removed from the surface, even though the charge associated with the anodic and cathodic portions of the waveform may suggest otherwise. Finally, consistent with niobium oxide removal during the cathodic pulse, an accumulation of niobium oxide powder on the cathode was observed, presumably deposited electrophoretically from the niobium oxide removed from the niobium coupon during the cathodic pulse. While much more work needs to be conducted to elucidate the exact nature of the anodic current transition, the anodic current transition appears to correlate strongly with effective electropolishing.

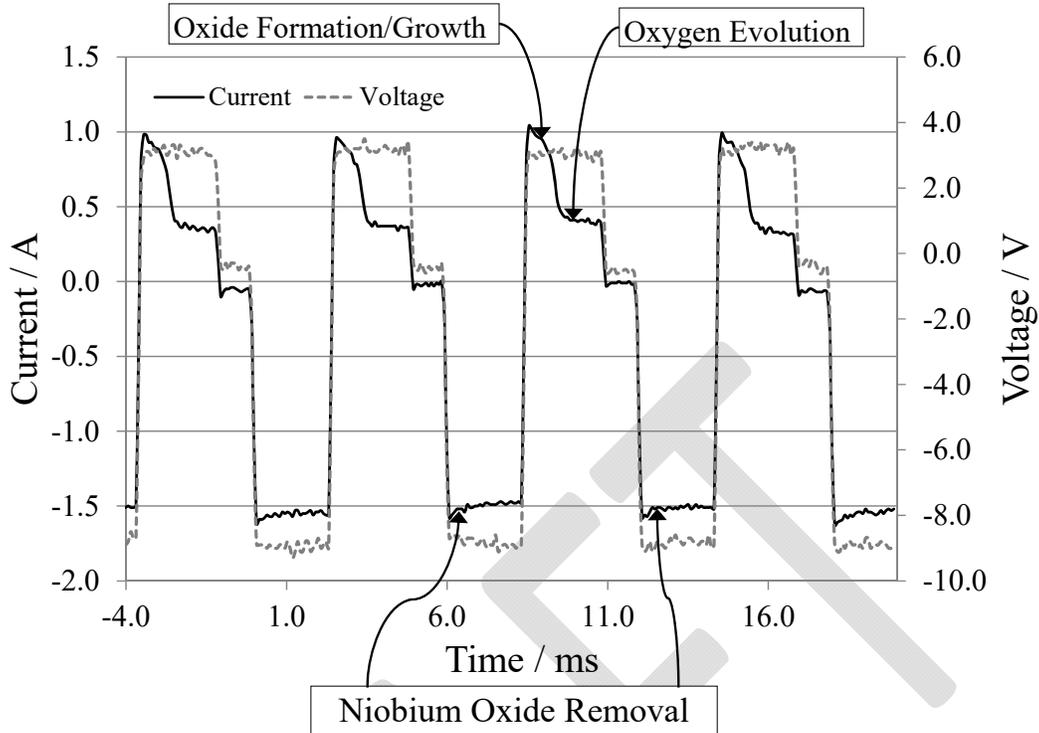
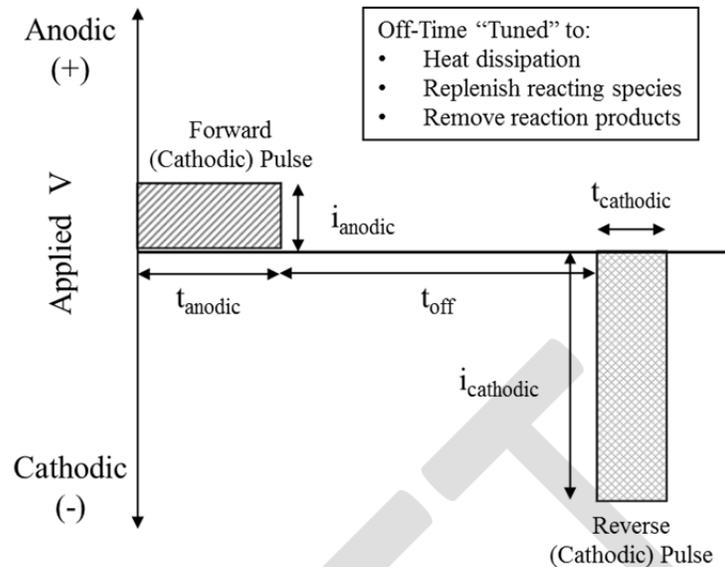


Fig. 21. Anodic current transition observed for effective electropolishing of niobium. Applied waveform: anodic pulse of 3 V for 2.5 ms, off-time of 1 ms, cathodic pulse of 9 V for 2.5 ms.

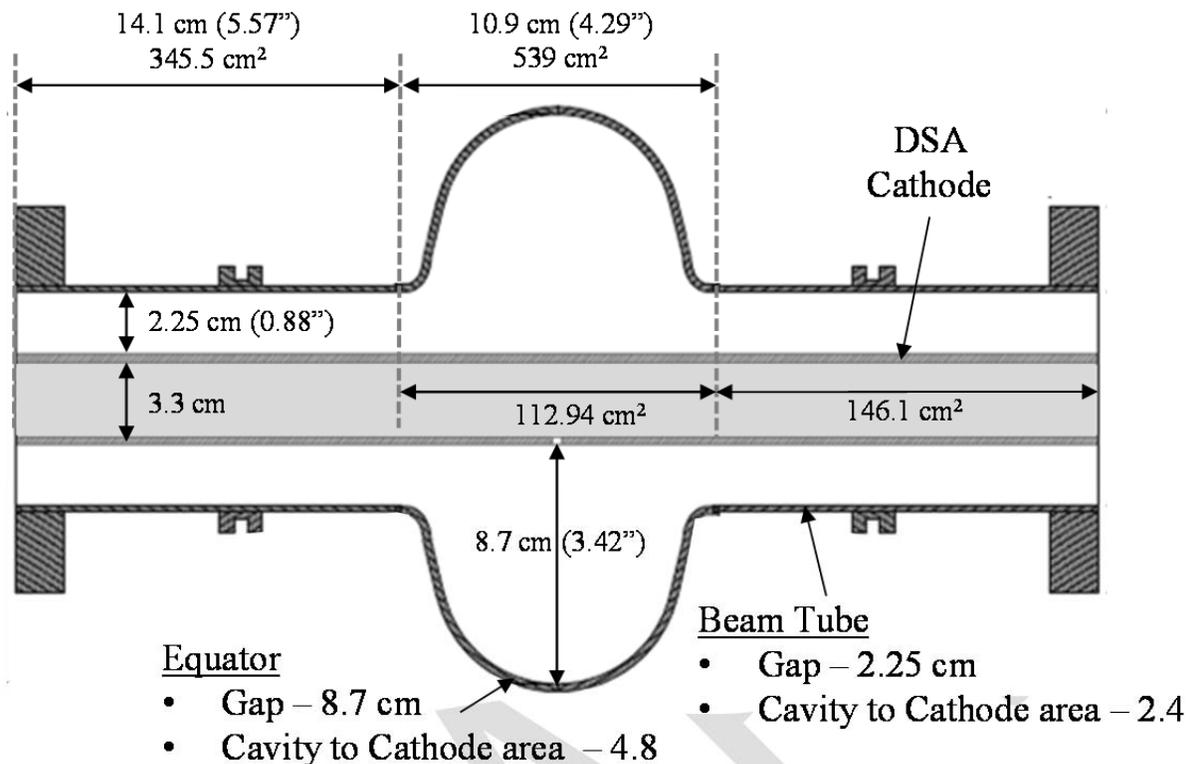
During the establishment of clean room and cavity processing apparatus, as well as the extensive pulse reverse voltage waveform study, word was received from Mr. Rowe (ARRA TPOC) that there was concern that the proposed approach would not lead to a practical solution due to the heat build-up during processing. This seemed unlikely since the anodic voltage pulses were typically 2 to 4 volts and the cathodic voltage pulses were ~10 volts in a relatively conductive electrolyte. This is in contrast to the DC process using ~18 volts in a relatively resistive electrolyte. However, in order to demonstrate that PRC waveforms could be designed to minimize heat build-up during processing, experiments were conducted using a high power waveform (30 V anodic and 35 V cathodic) in the bench-scale coupon cell where significant heating was observed during a short processing time. As shown in Fig. 22, increasing the off-time between pulses from 0.3 to 5 ms demonstrated that the heat could be dissipated, even after 560 minutes of operation. For the lower power waveforms that are currently being used, heat buildup can be effectively controlled. This demonstrates another strong advantage of the pulse/pulse reverse voltage approach to electropolishing.



t_{off} (ms)	Total Time (min)	T_i ($^{\circ}\text{C}$)	T_f ($^{\circ}\text{C}$)
0.3	40	15	33
0.6	120	14	35
1.0	120	14	28
5.0	560	16	19

Fig. 22. Elimination/minimization of heat build-up during pulse reverse voltage electropolishing by inserting longer pulse off-times.

With the development of pulse reverse voltage waveform parameters for electropolishing niobium coupons and within the constraints of commercially available rectifiers, attention was focused on transitioning the electropolishing process to single-cell SRF cavities. In addition to the difference in surface area between the 1"x1" and 3"x3" coupons and single-cell cavities, the geometry of the cavity was different. The geometric relationship between the cathode tool and the cavity was characterized by two regions; two cylindrical "beam tube" regions and one "equator" region, as shown in Fig. 23.



- ARRA purchase order did not allow studies on curved cavity sections.
- Coupon studies used to simulate **area ratios** and **gaps** representative of the **beam tube** and **equator**.

Fig. 23. Niobium SRF cavity geometry gaps and area ratios for the beam tube and equator regions.

In the beam tube regions, the cathode to cavity gap was 2.25 cm and the ratio of cavity area to cathode area was 2.4. In the equator region, the cathode to cavity gap was 8.7 cm and the ratio of cavity area to cathode area was 4.8. To “simulate” some of these geometrical aspects of the SRF cavity beam tube and equator regions, a limited number of experiments were conducted with flat coupons at gaps and anode to cathode area ratios representative of these regions. The resulting data suggested that in order to achieve effective polishing:

- 1) As the anode-cathode gap increases, the anodic transition time increases, and
- 2) As the anode-cathode surface area ratio increases, the anodic transition time increases.

With these observations, future efforts were focused on electropolishing of single-cell niobium SRF cavities. Subsequent review of this and additional data and new observations have suggested refinements to this model. However, at this early stage of development, these observations provided the basis for moving forward.

4.6 Transition Pulse Reverse Voltage Electropolishing to Niobium Superconducting Radio Frequency Cavities

Due to the expense, only four single-cell niobium SRF cavities could be provided by FNAL under the ARRA program. Specifically, a “developmental” single-cell cavity would be used to transition the pulse reverse voltage process to the niobium cavity by appropriate adjustment of the waveform parameters. The remaining three “performance” single-cell cavities were used to validate equivalent performance to single-cell cavities processed using the standard sulfuric/hydrofluoric acid process [77]. In addition, the ARRA purchase order stipulated that the single-cell cavities would be processed in the “standard” cavity processing apparatus based on the design specifications of Argonne National Laboratory/FNAL [75]. Therefore, the developmental cavity was processed in a horizontal orientation (Fig. 24) with ~60% of the volume filled with 5-10% (w/w) aqueous sulfuric acid and rotated at 1 revolution per minute per standard practice.

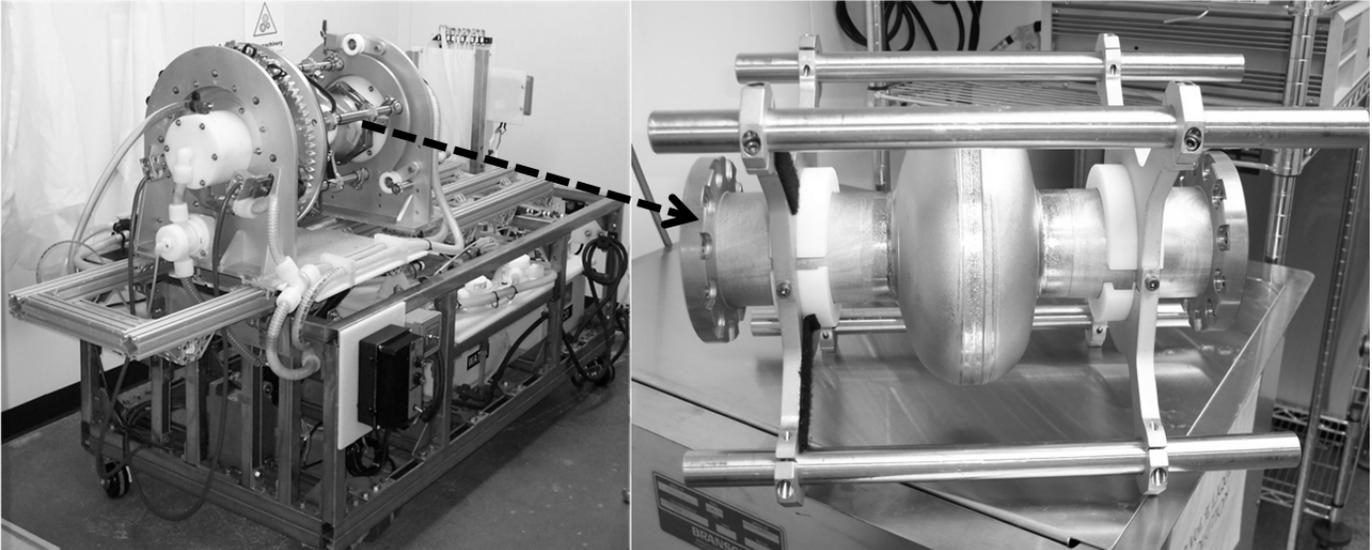


Fig. 24. SRF cavity processing apparatus with rotating horizontal cavity orientation and partially filled with electrolyte.

After approximately seven unsuccessful trials in the developmental cavity, based on visual observations, the original Siemens literature upon which current cavity processing is derived was revisited [78]. The current cavity electropolishing protocols (horizontal orientation, partial electrolyte fill, rotation) were developed for the highly viscous sulfuric/hydrofluoric acid solution where according the original Siemens patent;

the problem of,

“...electrolytic polishing hollow niobium bodies of a complicated geometrical structure...where development of gases...rise from the cathode...forming gas pockets...resulting in portions of the inside surface not polished...”

is solved by,

“...horizontally orienting the hollow niobium body...partially filling said hollow body with polishing solution and slowly rotating said hollow body...”

Since the viscosity of the low concentration sulfuric acid solution (~1 cp) is much less than that of the conventional sulfuric/hydrofluoric acid solution (~25 cp), it was speculated that the rotation rate used for the

high viscosity standard solution may not be optimal for the low viscosity solution. Furthermore, horizontal operation with partial cavity fill and rotation may not be required for the pulse reverse voltage niobium SRF cavity electropolishing process. Additionally, vertical cavity processing is simpler and due to capital cost considerations would be more desirable from an industrial perspective. Consequently, the cavity processing apparatus was positioned in the electrolyte “dump” mode and conducted additional electropolishing experiments with the cavity in a vertical orientation completely filled with electrolyte and without rotation (Fig. 25).



Fig. 25. SRF cavity processing apparatus operation in the “dump” mode oriented vertically without rotation and completely filled with electrolyte.

Additional pulse reverse voltage electropolishing trials were conducted on the developmental cavity in the vertically oriented dump mode without rotation and completely filled with electrolyte. In these additional developmental cavity trials, the waveform timing was adjusted to account for the increased anode to cathode gap and area ratios until the anodic current transition was observed as an indication of electropolishing. In addition, as shown in Fig. 26, regions of the cavity were progressively isolated to expose:

- 1) One beam tube region,
- 2) The equator region,
- 3) One beam tube and the equator regions,
- 4) The complete cavity, i.e. both beam tube regions and the equator.

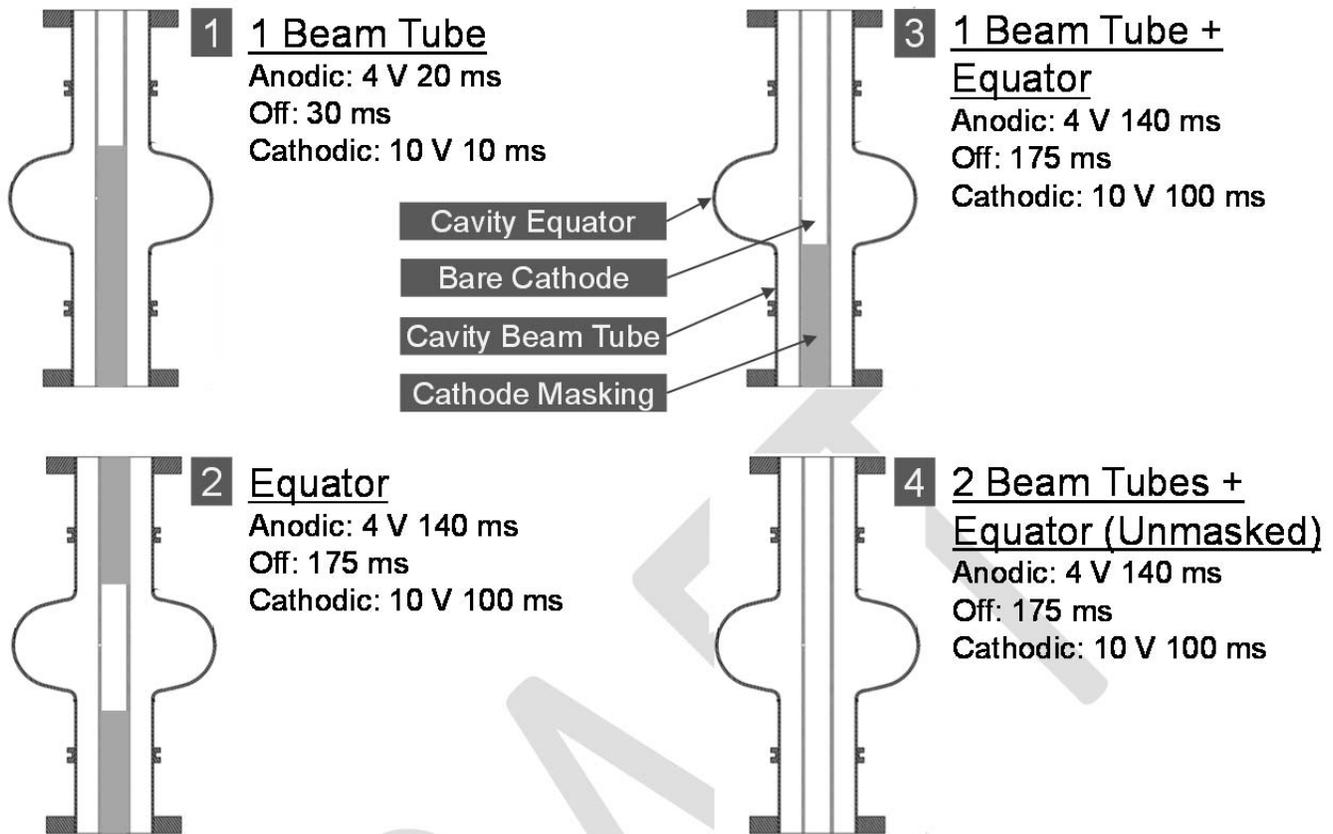


Fig. 26. SRF developmental cavity processing sequence. Shaded areas on the cathode indicate masking.

Consistent with the experimental observations of the effect of the electrode gaps and area ratios in the coupon studies, the anodic pulse period was extended in order to observe the anodic current transition in both the beam tube and equator regions. As shown in Fig. 27a, in the single beam tube test (#1) a single transition at a relatively short transition time was observed, from oxide formation in the beam tube to water electrolysis. In the equator only test (#2) a single transition at a relatively long transition time was observed, from oxide formation in the equator to water electrolysis. In the full cavity test (#4) two anodic transitions were observed: the first at a relatively short transition time from oxide formation in the beam tube to oxide formation in the equator, followed by a second transition from oxide formation in the equator to water electrolysis. These were termed the Beam Tube Transition and the Equator Transition.

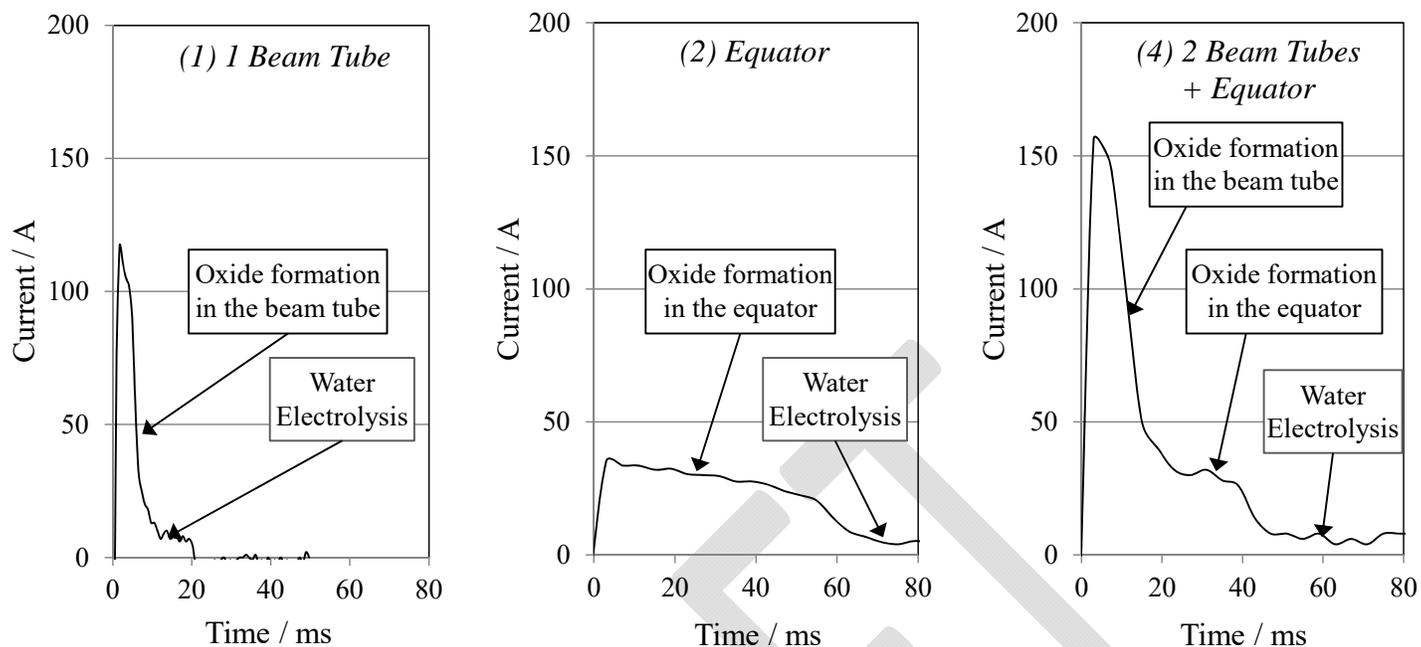


Fig. 27. Anodic current transitions for the SRF developmental cavity per the experiments shown in Fig. 26: 1) beam tube only, 2) equator only, and 4) 2 beam tubes + equator. Note, for clarity, the anodic and cathodic voltage pulses and cathodic current responses are not shown.

When the anodic current responses were overlaid (Fig. 28) for each of the four trials in the developmental cavity (Fig. 26), the observation was made that as the total area exposed increased, the Beam Tube Transition time increased, while the Equator Transition time decreased. Based on the difference in anode to cathode gap and area ratio at the beam tube versus the equator, this suggests that the beam tube dominates the geometric current distribution over the equator. This would result in some non-uniformity in removal from the beam tube to the equator, and in fact that has been observed in the pulse reverse cavity electropolishing experiments as well as conventional practice [79].

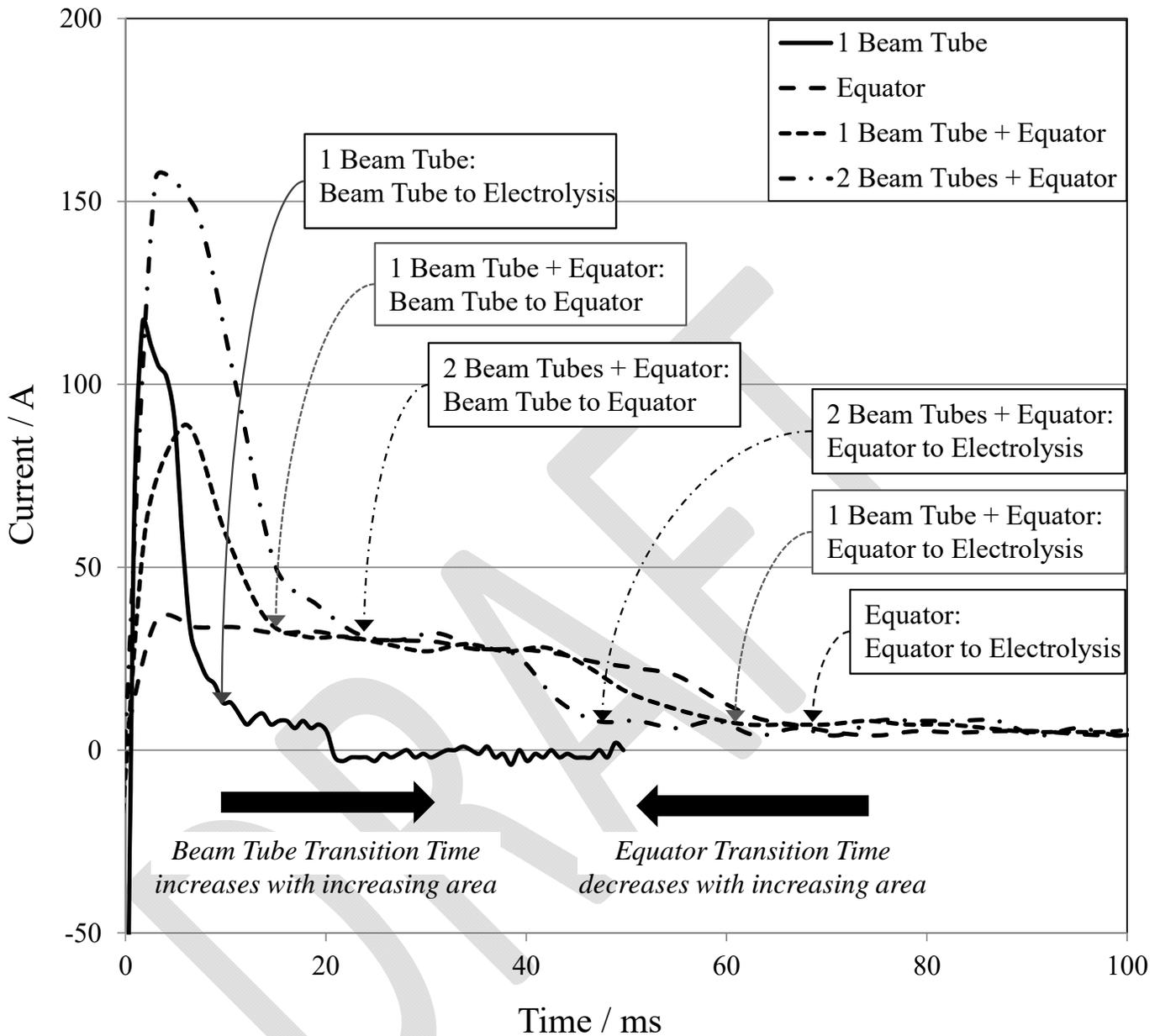


Fig. 28. Anodic current transition times for SRF developmental cavity processing sequence described in Fig. 26. Note, for clarity, the anodic and cathodic voltage pulses and cathodic current responses are not shown.

After electropolishing the complete single-cell cavity, visual inspection indicated acceptable electropolishing and this was confirmed at FNAL [80]. At least from a visual inspection perspective, the coupon study observations proved critical in developing the appropriate pulse period. Subsequently, additional analysis of the coupon experimental data would provide further observations of the impact of anodic and cathodic pulse charge on niobium electropolishing [81]. With the acceptable visible electropolishing confirmed, “performance” cavities were sent by FNAL for electropolishing. All subsequent performance cavity processing trials were conducted with the cavity in a vertical orientation, filled with electrolyte and without rotation.

The first performance cavity had previously been processed using the standard two-step surface finishing protocol of buffered chemical polishing followed by electropolishing. The cavity superconducting and accelerating gradient characteristics were validated at FNAL prior to sending the cavity to Faraday, where “light” electropolishing was conducted to remove ~ 30 μm of material. The cavity was sent back to FNAL and the cavity superconducting and accelerating gradient characteristics were verified to be within the acceptable range of cavities subjected to the standard surface finishing protocols [80]. This experiment demonstrated that the pulse reverse voltage electropolishing process did not adversely impact niobium SRF cavity performance.

The second performance cavity had not been processed using the standard surface finishing protocol and did not exhibit acceptable superconducting and accelerating gradient characteristics. “Heavy” electropolishing was conducted whereby ~ 100 μm of material was removed. The superconducting and accelerating gradient characteristics were evaluated at FNAL and the cavity superconducting and accelerating gradient characteristics were verified to be within the acceptable range of cavities subjected to the standard surface finishing protocols [80]. In addition, the cavity exhibited “Q-disease”, which is indicative of hydrogen uptake and generally occurs during bulk ($> \sim 50$ μm) material removal. In conventional cavity processing, Q-disease is eliminated with a high temperature (~ 800 C) bake after bulk material removal [80]. “Light” material removal with the conventional electropolishing process does not result in Q-disease. While at FNAL, this cavity was subjected to the standard high temperature bake and the Q-disease was eliminated. This cavity was returned for “light” electropolishing with ~ 20 μm material removed. Subsequent testing at FNAL demonstrated that “light” material removal with the pulse reverse voltage electropolishing process similarly does not result in Q-disease [80].

The third and last performance cavity had previously been processed using the standard two step surface finishing protocol and was identified as a “high performing” cavity by FNAL. “Light” electropolishing was conducted whereby ~ 25 μm of material was removed. After evaluation of the superconducting and accelerating gradient characteristics, FNAL reported that this cavity exhibited the highest performance of any cavity evaluated at FNAL [80]. While the source of this exceptional performance is not clear, this observation along with the observations on the previous performance cavities validate the applicability of pulse reverse voltage surface finishing for electropolishing niobium SRF cavities in a simple eco-friendly aqueous electrolyte [82]. Due to the lower capital and operating costs, the pulse reverse voltage electropolishing process is estimated to cost approximately 20% of the cost of the conventional process [83].

In summary, an electrochemical polishing process for niobium superconducting radio (SRF) frequency single-cell cavities based on pulse reverse current/voltage (PRC) principles has been demonstrated. The use of PRC enables a low-viscosity/low acid concentration aqueous electrolyte, which does not require hydrofluoric acid. This development activity occurred over a period of approximately 5 years, and the PRC-based process has been demonstrated to yield at least equivalent SRF cavity performance to the conventional process based on DC electrochemical polishing using high-viscosity/high acid concentration 9:1 sulfuric/hydrofluoric acid electrolyte. While some in the community accepted the potential of PRC electrochemical polishing of flat niobium coupons as fundamentally paradigm-changing, it took the demonstration of single cell niobium cavity polishing and performance demonstration for the PRC electrochemical polishing process to be more widely embraced. With this successful demonstration, confidence in the ability of the PRC electrochemical polishing process to replace the current process is growing and work is ongoing independently or collaboratively with several DOE as well as international high energy physics facilities to further advance the PRC electrochemical polishing technology. A next step is to better understand the effects of anode to cathode gap and area ratios; another is to manipulate the geometry of the electrochemical polishing cell by shielding to get more uniform geometric current distribution throughout the cavity. It must be noted that while a pulse reverse waveform can

influence the balance of primary, secondary and tertiary current distribution at the microscale, it cannot overcome the effects of inefficient cell design. Ongoing work with curved sections, half cavity cells, and investigation of the effects of flow on the boundary layer throughout the cavity, as well as further manipulation of the pulse reverse waveform will all lead to a better understanding of the suggested cathodic electropolishing mechanism and the optimization of the PRC electrochemical polishing process. These activities will lead to a demonstration of the PRC electrochemical polishing process on nine-cell niobium SRF cavities, which are a key component of accelerator technology.

5 Concluding Thoughts

Observations and milestones over a period of twenty-two years describe the development of pulse/pulse reverse current processes that have led to simpler plating, deburring and metal finishing chemistries and the development of a new “eco-friendly” pulse reverse voltage electropolishing process for niobium SRF cavities. These developments required a paradigm shift in electrochemical plating and surface finishing processes, specifically with respect to replacing the conventional reliance on additive and sometimes toxic chemistries for process control with the use of simple chemistries and pulse reverse electric fields. Guiding principles based on seminal works from the early development of pulse and pulse reverse plating has resulted in approximately 30 patents covering various embodiments pulse and pulse reverse plating and surface finishing.

The first success in identifying and taking advantage of this paradigm shift and these guiding principles was in pulse reverse plating of copper, where plating performance and deposit properties were improved with the application of pulse reverse current and a reduction in chemical additives. The recognition that the pulse reverse electric field may obviate the need for chemical additives in plating processes was then applied to a wide range of anodic processes. Initially, deburring of non-passive materials using forward only anodic pulses was demonstrated. This approach was derived based on observations of localized current distribution during pulse plating of lead frame contacts for electronics applications. Subsequently, electropolishing of passive materials was demonstrated by incorporating a cathodic reverse pulse to remove the adverse effects of passive film formation. This approach was derived based on observations of elimination of adverse hydrogen evolution effects during pulse reverse plating of low faradaic efficiency materials such as trivalent chromium. From this accumulated knowledge, the pulse reverse voltage approach was successfully applied to strongly passive materials such as niobium. Finally, the pulse reverse voltage electropolishing process was transitioned to niobium SRF cavities based on the key observation that electropolishing correlated with an anodic current transition during the anodic voltage pulse.

Conventional direct voltage electropolishing of niobium SRF cavities utilizes a concentrated mixture of sulfuric and hydrofluoric acid and is understood to mechanistically function as described by the Jacquet “viscous salt film” model. Pulse reverse voltage electropolishing uses low concentration aqueous sulfuric acid electrolyte devoid of hydrofluoric acid and is not easily rationalized with the viscous salt film model. As such, a paradigm shift or modification to the Jacquet model is emerging. While additional work is required to elucidate the mechanistic aspects of the pulse reverse process, this process is tentatively referred to as “cathodic electropolishing.”

Upon its founding in 1991, Faraday was focused solely on the development of cathodic/electrodeposition processes using pulse current and pulse reverse current principles. Over time, lessons learned in cathodic

processes were successfully applied to developing pulse and pulse reverse anodic processes and thus broadened the company's mission. These lessons learned will continue to be applied, as new electrochemical engineering technologies are investigated and developed in many other fields. The experience gained over twenty years of research and development suggests that scientists, engineers and technologists should conduct their research and development activities with a careful balance between current fundamental understandings combined with a willingness to pursue evolving observations that do not necessarily fit existing paradigms. Finally, this discussion concludes with a quote by Eliezer Gileadi, Professor of Chemistry at Tel-Aviv University, a long-time friend and colleague, which is displayed in Faraday's lobby and serves as a guiding principle [84]

"...in order to create, one must first question that which exists..."

Acknowledgements

The authors gratefully acknowledge the U.S. Small Business Innovation Research and Small Business Technology Transfer (SBIR/STTR) programs of the Department of Energy (DOE), National Science Foundation (NSF), Environmental Protection Agency (EPA), Department of Defense (DoD), National Institutes of Health (NIH) for providing the seed funding, which contributed to the advancements of pulse and pulse reverse electrochemical technologies. The authors also acknowledge the technology development funding of Ford Motor Company, Swagelok Corporation as well as numerous confidential commercial clients and licensees. Specifically regarding the niobium electropolishing activities, the authors gratefully acknowledge the financial support and guidance of 1) DOE Program Manager Dr. Manouchehr Farkhondeh (SBIR Phase I Grant No. DE-SC0004588), 2) DOE Program Manager Dr. L. K. Len (SBIR Phase I Grant No. DE-FG02-08ER85053), 3) DOE Program Manager Mr. Allan Rowe (America Reinvestment in Research Act (ARRA) under DOE Fermi National Accelerator Laboratory (FNAL) P.O. No. 594128), 4) DOE Program Manager Dr. Manouchehr Farkhondeh (SBIR Phase I/II Grant No. DE-SC0011235), 5) DOE Program Manager Dr. Kenneth R. Marken, Jr. (SBIR Phase I/II Grant No. DE-SC0011342). In addition, the authors would like to acknowledge the technical guidance regarding SRF cavity processing, Dr. Charles Reece of the DOE Thomas Jefferson National Accelerator Facility, Mr. Allan Rowe of the DOE Fermi National Accelerator Laboratory, and Dr. John Mammosser and Dr. Jeff Saunders of the DOE Oak Ridge National Laboratory. The authors also acknowledge Prof. Der-Tau Chin of Clarkson University, Prof. C. C. Liu and Prof. Robert Savinell of Case Western Reserve University, Prof. Alan C. West of Columbia University and Prof. John Fortman of Wright State University, as well as numerous other university collaborators. Finally, the authors also acknowledge prior Faraday employees for their contributions to our pulse/pulse reverse electrochemical activities.

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