Electropolishing and Throughmask ElectroEtching of Nitinol Stents and Other Materials in an Aqueous Electrolyte

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Abstract

This paper will discuss the results of a Phase I NIH SBIR grant, aimed at demonstrating the feasibility of the FARADAYIC ElectroPolishing and Throughmask ElectroEtching processes for the fabrication of nitinol stents. The Throughmask ElectroEtching technology is being developed to enable rapid stent fabrication while maintaining pattern fidelity in a low-concentration, aqueous electrolyte. This process does not impart thermal damage to the stent, eliminating the need for descaling of undesired oxides. The objective of the work was to demonstrate the feasibility of this process with etch rates of >25 μm/min for patterns with strut widths of 50 to 100 μm and slot widths of 38 to 400 μm. A critical process step in conventional stent manufacturing is electropolishing, which is typically done in an electrolyte such as sulfuric/phosphoric acid. Faraday has considerable experience in electropolishing materials in simple, low concentration aqueous electrolytes using pulsed electrolytic fields tuned to the material of interest to achieve the desired surface finish. This process has been applied to a number of advanced engineered materials including stainless steel semiconductor valves and nickel and titanium based aerospace turbine components. This process could be equally applied as the final finishing step for any stent fabrication method, and will likely utilize the same electrolyte that will be used for the FARADAYIC ElectroEtching process. The results presented will discuss: 1) dimensional tolerance, 2) etch rate, and 3) surface finish. This effort is designed to transition into a Phase II program, in which a range of stent designs would be manufactured, in pilot-scale equipment.

Introduction

Electropolishing is an industrially important edge and surface finishing technology, especially as it pertains to polishing medical devices and implants, such as nickel-titanium medical implant stents. Conventional surface finishing technologies utilize high viscosity and/or low conductivity electrolytes, such as concentrated acids (e.g. sulfuric, phosphoric) and non-aqueous solutions (ethylene glycol, methanol-sulfuric acid).[1] For strongly passive materials (e.g. titanium and titanium alloys and niobium), hydrofluoric acid is added to the electrolyte to depassivate the surface.[2,3,4] Alternatively, some have suggested electropolishing strongly passive materials in acid-alcohol electrolytes with low water content[5] or organic solutions containing fluoride salts.[6] Due to the nature of conventional edge and surface finishing electrolytes, process control and robustness are difficult[7] and reject rates are often as high as 40 to 50%.[8,9]

Conventional Electropolishing

As depicted in Figure 1a, on some scale, all surfaces are rough. Electropolishing is the process whereby the asperities are preferentially removed by an electrolytic reaction (Figure 1b), generally represented as:

$$M^0 \rightarrow M^+ + e^- \qquad (1)$$

Low conductivity electrolytes, such as ethylene glycol may be used to focus the electric field on surface asperities as illustrated in Figure 2. As the electrolyte resistance is increased, the voltage gradient between the asperities and the recesses becomes greater and the asperities are preferentially removed. High resistance electrolytes have been particularly reported for electrochemical deburring applications. Due to the high electrolyte resistance required to focus the current field on the peaks, excessive heating of the electrolyte is often observed and there is a need for chilling during processing. Even with active chilling, during production trials for deburring automotive parts using an ethylene glycol electrolyte with ammonium salt additions, Ford Motor Co. reported excessive heat leading to an unacceptable ammonia

odor, limited cathode lifetime, and that the electrolyte was difficult to maintain and expensive to replace.[10]

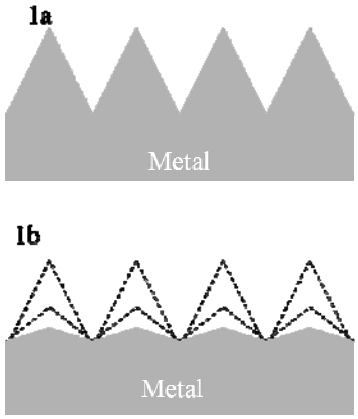

Figure 1. Generalized Surface Roughness (a) and Electropolishing by Removal of Asperities (b).

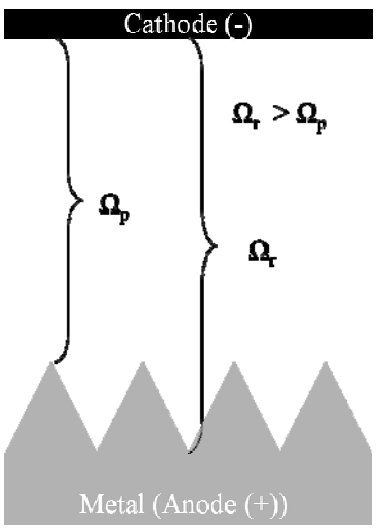

Figure 2. Focusing Electric Field on Surface Asperities in Low Conductivity Electrolytes.

As illustrated in Figure 3, high viscosity electrolytes are used in conventional electropolishing processes to focus the electric field on surface asperities. For given electrolyte agitation conditions, the diffusion layer thickness (δ) is proportional to the electrolyte viscosity. For diffusion layers thicknesses greater than the characteristic dimension of the surface roughness, under mass transport control, the currents will be higher at the asperities than the recesses and the asperities are preferentially removed. Jacquet first reported that the optimum region for electropolishing is the mass transport or current limited plateau in the polarization curve.[11] Subsequently, Wagner reported "microprofile" leveling under mass transport limited conditions for the case of large diffusion layers.[12] The diffusion limited process has been attributed to diffusion of the dissolved metal ion away from the polished surface[13] or the diffusion of an "acceptor ion" or complexing/solvating species to the polished surface.[14] These diffusion limited processes are further hindered, and hence electropolishing improved, by the formation of a viscous salt film in the recesses of the surface.[1]

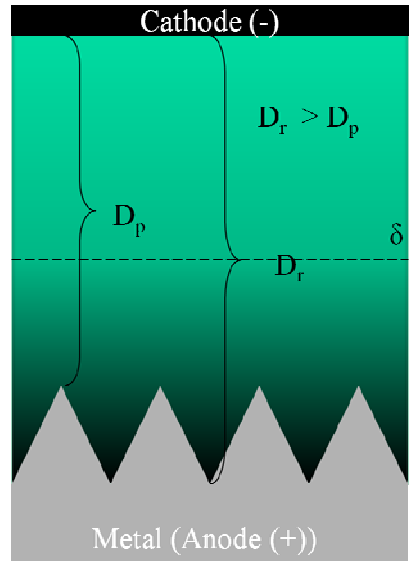

Figure 3. Focusing Electric Field on Surface Asperities in High Viscosity Electrolytes.

During anodic metal dissolution (eq. 1) some metal surfaces can form a passive oxide film, generally described as:

$$M + xH_2O \rightarrow M(O_x) + 2xH^+ + 2xe^- \qquad (2)$$

For these strongly passivating metals (stainless steel 300 series, titanium and nickel and their alloys among other materials), continued electropolishing leads to a roughened surface similar to pitting corrosion. Consequently, for some of these materials, hydrofluoric acid is added to the electrolyte to depassivate the metal surface by forming soluble metal fluorides and/or metal oxiflourides.[2,3] Considerable process control issues as well as safety issues are associated with managing and handling these hydrofluoric acid containing electrolytes.

In summary, conventional electropolishing processes using concentrated viscous acid electrolytes and/or resistive electrolytes and/or hydrofluoric acid electrolytes along with various chemical additives are complex and difficult to control. In the case of niobium superconducting radio frequency cavities and nickel-titanium stents, the reject rates associated with the conventional electropolishing process are as high as 40 to 50%.[8,9] Consequently, these is a need for an electropolishing process using non-viscous, conductive, simple aqueous electrolytes devoid of hydrofluoric acid or other difficult to control additives.

Pulse/Pulse Reverse Electropolishing in Non-Viscous Electrolytes

We have developed and continue to develop surface finishing processes based on pulse/pulse reverse electrolysis utilizing simple, easy to control aqueous electrolytes.[15] Figure 4 is a generalized pulse/pulse reverse waveform for electropolishing. The anodic pulse is tuned (pulse-time and peak voltage) to enhance mass transport and control current distribution. The cathodic pulse is tuned to depassivate the surface and thereby eliminate the need for hydrofluoric acid or other oxide removing chemical additions. An off-time may be inserted between the pulses to facilitate replenishment of reacting species and removal of byproducts and heat. While the pulse/pulse reverse waveform contains off-times and cathodic pulses, the material removal rate during pulse/pulse reverse electropolishing is generally higher than or equal to that obtained under the direct current (DC) electropolishing. This is because the instantaneous anodic pulse current is much higher than the steady state current obtained under DC conditions and compensates for off-times and cathodic periods such that the average material removal rate (net anodic current density) is equivalent to or greater than DC electropolishing.

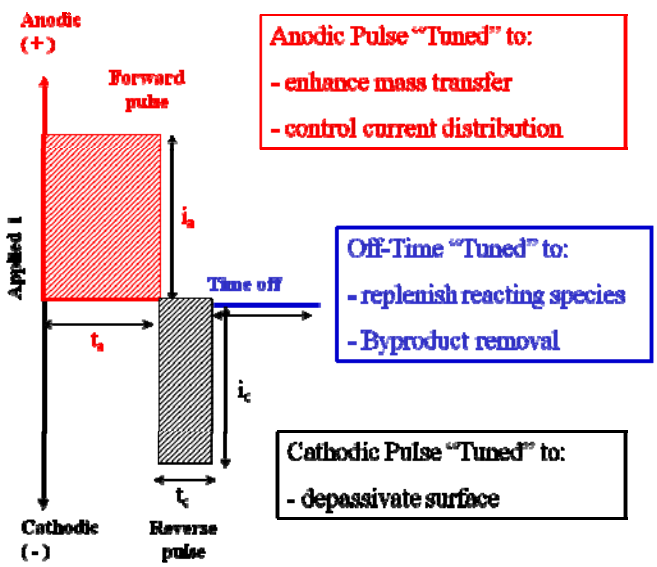

Figure 4. Generalized Pulse/Pulse Reverse Waveform for Electropolishing.

Key to the development of the pulse/pulse reverse waveform is the "tuning" of the anodic and cathodic pulses (pulse time and pulse amplitude) as well as the selection of the duration of the off-times. While pulse/pulse reverse waveform parameters cannot be selected *a priori*, we have developed a series of guiding principles for optimizing the pulse/pulse reverse waveform parameters for a particular application. These guiding principles are summarized below.

By considering the theoretical developments associated with voltage-current responses as a function of time resulting from a single pulse, the concentration profile from the electrode surface to the bulk solution consists of a stationary layer (δ_s) and an inner "pulsating" layer (δ_p).[16,17,18] As the pulse time is decreased, the thickness of inner pulsating layer becomes smaller, as illustrated in Figure 5. Assuming linear concentration gradients and conducting a simple mass balance, the inner pulsating layer is proportional to the pulse-time (t_p) of the pulse:[17]

$$\delta_p = 2((Dt_p)/\pi)^{1/2} \qquad (3)$$

where D is the diffusion coefficient. More exacting estimates of the thickness of the inner pulsating diffusion layer have been proposed,[18] but the key point is the proportionality with pulse-time. Since the inner pulsating layer is proportional to the pulse-time, we refer to the pulsating layer as the "electrodynamic diffusion layer".[19] Just as the thickness of hydrodynamic diffusion layer (Nernst diffusion layer) may be adjusted by changing the solution viscosity and/or solution agitation, the electrodynamic diffusion layer may be adjusted by the pulse-time.

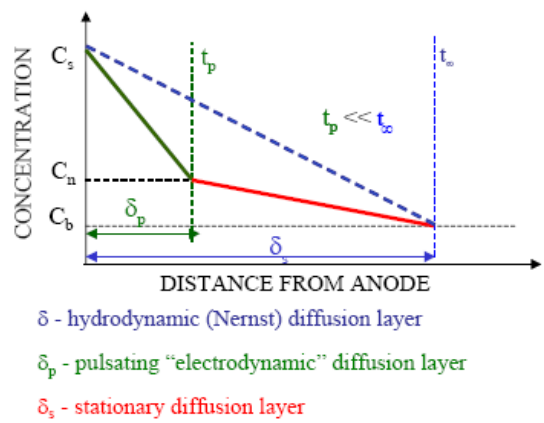

Figure 5. Linearized Hydrodynamic, Stationary, and Pulsating Diffusion Layers.

In electropolishing, the diffusion layer thickness is relevant in context with the roughness scale of the surface. A microprofile is the case where the diffusion layer thickness is larger than the roughness scale. For electrolysis under microprofile conditions and under mass transport control, the peaks are preferentially removed relative to the recesses and electropolishing is achieved. A macroprofile is the case where the diffusion layer thickness is less than or equal to two times the roughness scale and consequently the diffusion layer follows the surface contour. For electrolysis under macroprofile conditions and under mass transport control, the peaks and recesses are equally removed and the surface roughness generally remains unchanged. That is, electropolishing is not accomplished.

Whether or not the electropolishing process is under mass transport control is determined by the relationship between the pulse-time (t_p) and the transition time (τ).[18] Although originally developed for electrodeposition, for electropolishing the transition time may be thought of as the time for the dissolved metal to reach its solubility limit at the electrode surface. The transition time is quantified by the Sand equation

and is inversely proportional to the peak current density (i_{peak}) for single current pulses.

$$\tau = \pi((nF)^2CD^2)/4i_{peak}^2 \qquad (4)$$

Where n is the number of electrons taking place in the reaction, F is Faraday's constant and C is the bulk concentration of the reacting species. For cases where the pulse-time is approximately equal to or greater than the transition time, the electrolytic process is under mass transport controlled conditions.[20] Conversely, for cases where the pulse-time is substantially less than the transition time, the electrolytic process is not under mass transport control.

We assume that these relationships from single pulse studies are applicable to anodic pulse waveforms with off-times and interspersed anodic/cathodic waveforms with off-times. For electropolishing under macroprofile diffusion layer conditions, the pulsed anodic waveform converts the macroprofile diffusion layer to a smaller electrodynamic macroprofile diffusion layer (Figure 6). For shorter and shorter anodic pulse-times, the electrodynamic macroprofile diffusion layer will be smaller and smaller (see eq. 3). At the same material removal rate, the contribution of mass transport will be less for the smaller electrodynamic macroprofile and the material removal will occur preferentially at the peaks. This is due to the fact that the process is less influenced by mass transport and the current distribution is therefore more non-uniform, all else being equal.[20,20] Consequently, we have generally found for macroprofile cases, it is desirable to have relatively short anodic pulse-times.

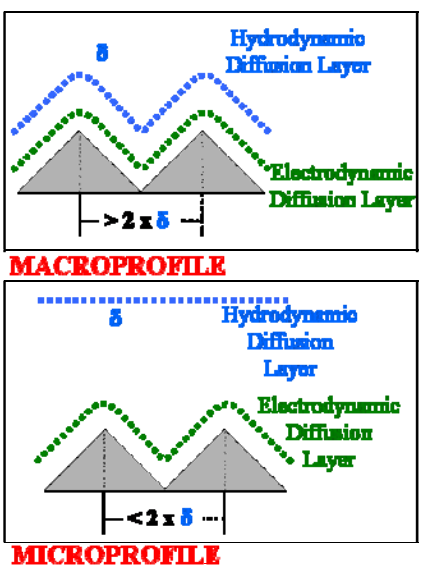

Figure 6. Representation of Hydrodynamic and Electrodynamic Diffusion Layers for a Macroprofile and a Microprofile.

For electropolishing under microprofile diffusion layer conditions, the pulsed anodic waveform converts the microprofile to a smaller microprofile or to a macroprofile (Figure 6). We have generally found for cases where a microprofile is converted to a smaller microprofile, it is desirable to have relatively high peak current densities in order to have relatively short transition times. In this manner, we maintain mass transport control and the current distribution is more non-uniform and preferentially focused on the peaks. We have generally found for cases where a microprofile is converted to a macroprofile, it is desirable to maintain relatively low peak current densities in order to have relatively long transition times. In this manner, we remove mass transport control and the current distribution is more non-uniform and preferentially focused on the peaks.

In summary, the pulse-time is proportional to the electrodynamic boundary layer thickness and the amplitude of the pulse is inversely proportional to the transition time. For pulse-times substantially less than the transition time, the electrolytic process will not be under mass transport control. For pulse-times approximately equal to or greater than the transition time, the electrolytic process will be under mass transport control. A macroprofile diffusion layer situation is more likely to occur at the beginning of the electropolishing process and a microprofile diffusion layer occurs as the electropolishing process progresses. An understanding of these effects provides the user with a set of guiding principles to optimize the waveform parameters of the electropolishing process for a given application.

The final consideration for developing a pulse/pulse reverse electropolishing waveform is for the case of passive materials. For these materials, anodic only pulses lead to a rougher surface due to the non-uniform breakthrough of the passive film.[21,22] In order to depassivate the surface, we intersperse cathodic pulses within the anodic pulses in place of or in conjunction with the off-times.[23,24,25] In a general sense, we assume the cathodic pulse remove the oxide film and restore the virgin metal surface as the reverse of reaction (2).The amplitude of the cathodic pulses is selected to remove the passive metal-oxide film and is generally material specific. For metals with stronger oxide films, higher cathodic amplitudes are required. As noted above, some have suggested using non-aqueous or low water content electrolytes to remove the source of oxygen (eq. (2)) leading to the formation of the passive film. However, from an industrial implementation perspective, these processes are difficult to control due to the resistivity and hydroscopic nature of the non-aqueous electrolyte.

Results

Nickel-Titanium Alloy

Nitinol is an intermetallic of approximately 50% nickel and 50% titanium. Due to Nitinol's shape memory effect, ductility, corrosion resistance and fatigue strength, Nitinol has applications including actuators, dental orthodontics and medical stents. In the case of medical stents, after cutting the stent pattern from a Nitinol tube with a laser, the stent is typically electropolished in a chilled solution of concentrated

viscous phosphoric acid. This conventional electropolishing process often yields reject rates of 40 to 50%.[8]

We are developing a pulse/pulse reverse for electropolishing and electrochemical through-mask etching of Nitinol materials. Based on preliminary polarization studies, we selected 30 wt% aqueous sulfuric acid electrolyte.[26] The samples used in these preliminary studies were patterned Nitinol coupons with lines and spaces of varying dimensions. Due to the feature size of the lines and spaces, we assumed that the process was operating under a microprofile. For electrochemical through mask etching, these conditions dictated short anodic pulses of relatively high voltage amplitude[27] with interspersed cathodic pulse of moderately high amplitude to depassivate the strongly passive surface oxide. Although we have only conducted preliminary experiments with Nitinol, the initial results indicate we can obtain a mirror-like finish (R_q ~0.1 µm) and good pattern fidelity (Figure 12). Due to the simple nature of the aqueous electrolyte and absence of hydrofluoric acid or other fluoride salts to depassivate the surface, we are encouraged that a robust, cost-effective process can be developed for electropolishing Nitinol materials with low reject rates.

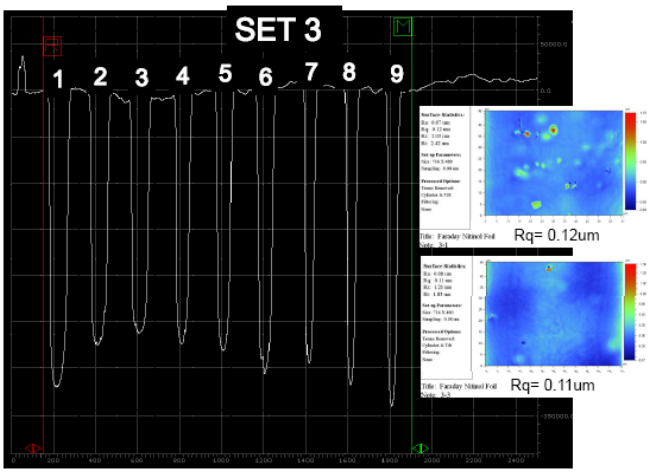

Figure 7. Electrochemical Through-Mask Etching of Patterned Nitinol Coupons.

Niobium

Niobium is the material of choice for superconducting radio frequency (SRF) cavities used in linear particle accelerators. In order to meet the performance requirements, approximately 125 µm of material must be removed from the internal surface of the SRF cavity. A two step process is currently used. Buffered chemical polishing is used to remove approximately 100 µm of material resulting in an R_a of approximately 2 to 5 µm. Electropolishing is then used to remove an additional 25 µm of material to achieve a final surface finish with an Ra of less than 0.2 µm. The electropolishing electrolyte is approximately nine parts sulfuric acid (98%) to one part hydrofluoric acid (48%).[2] The process requires special maintenance and handling precautions due to the use of hydrofluoric acid and is difficult to control with approximately 50% of the electropolished SRF cavities exhibiting pits or other surface defects limiting SRF cavity performance.[9]

We are developing a pulse/pulse/reverse electropolishing process for niobium SRF cavities. In preliminary work, we are developing process parameters using niobium coupons. Our generalized pulse reverse waveform utilizes a short anodic pulse followed by a short cathodic pulse with a relatively long off-time to facilitate heat removal. Our electropolishing electrolyte is aqueous sulfuric acid (~30 wt%) devoid of hydrofluoric acid and other additives. From preliminary coupon studies we have achieved a mirror-like surface finish free of defects (Figure 13). R_a values were measured ranging from approximately 0.004 µm to 0.001 µm to 0.0004 µm for scan sizes of 50x50 µm, 10x10 µm, and 2x2 µm, respectively. We are continuing to develop pulse/pulse reverse wavefrom parameters and scaling the process from coupons to single-cell SRF niobium cavities. The aqueous sulfuric acid electrolyte devoid of hydrofluoric acid offers considerable promise for a robust, low cost, safe electropolishing process for SRF niobium cavities.

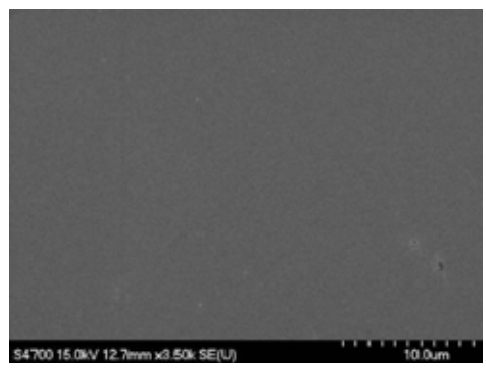

Figure 8. Surface Image of Electropolished Niobium Coupon.

Summary and Conclusion

We have described a pulse/pulse reverse electropolishing process using aqueous electrolytes. We presented guiding principles for pulse/pulse reverse waveform development. These include the proportionality of the pulse-time to the electrodynamic diffusion layer and the inverse relationship of the pulse amplitude to the transition time. Additionally, the relationship of the diffusion layer thickness to the surface asperity characteristic roughness determines a macroprofile or microprofile condition. Finally, for passive materials, cathodic pulses are interspersed to depassivate the surface and off-times may be used to facilitate heat removal. These concepts combined with an understanding of current distribution allow one to develop the appropriate pulse/pulse reverse waveform without undo experimentation. Applications for electropolishing of nitinol (nickel-titanium alloys) and niobium coupons were presented with surface roughnesses ranging from R_a of approximately 0.12 µm (nitinol) to 0.004-0.0004 µm (niobium). Due to the low viscosity/high

conductivity nature of the electrolyte and the absence of hydrofluoric acid our other chemical additives, the pulse/pulse reverse electropolishing is robust, low cost and safe.

Acknowledgements

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