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Electropolishing of Passive Materials in HF-Free Low Viscosity Aqueous Electrolytes

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A pulse reverse electrochemical surface finishing process for electropolishing passive materials is described. Unlike conventional electrochemical surface finishing processes, the pulse reverse process does not require low conductivity/high viscosity electrolytes and does not require the addition of chemical species to remove the passive film associated with electropolishing of passive and strongly passive materials. This paper focuses on pulse/pulse reverse electropolishing of niobium.
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On some scale, all surfaces are rough. Electropolishing is the process whereby the asperities are preferentially removed by an electrolytic reaction, which may be generally represented as:

$$M^0 \rightarrow M^{+n} + ne^- \quad [1]$$

For large asperities, generally defined as features larger than $\sim$1 μm,[1] low conductivity electrolytes are used to affect the primary current distribution such that the voltage gradient between the asperities and the recesses of the surface is magnified, and the asperities are preferentially removed. High resistance electrolytes are generally reported for electrochemical removal of large features, such as deburring applications.[2,3] For small asperities, generally defined as features smaller than $\sim$1 μm,[1] high viscosity electrolytes are used to affect the tertiary current distribution such that under mass transport control the limiting currents are higher at the asperities than in the recesses and the asperities are preferentially removed. Jacquet[4] was one of the first to report that the optimum region for electropolishing is the mass transport or current limited plateau in the polarization curve.

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

$$M + xH_2O \rightarrow M(O_x) + 2xH^+ + 2xe^- \quad [2]$$

For these strongly passivating metals (e.g. stainless steels, titanium, nickel, niobium, and their alloys), continued electropolishing under direct current (DC) electric fields in a simple electrolyte can lead to a roughened surface similar to pitting corrosion. To remove the passive film, aggressive chemicals are added to the electrolyte to remove the passive film. For example, in the case of niobium, hydrofluoric acid is added to the electrolyte to depassivate the surface.[5] In addition to the electrolyte handling and safety issues associated with concentrated hydrofluoric acid, conventional DC electropolishing of niobium presents process control issues, and reject rates are often 40 to 50%.[6] In this paper, we describe a pulse reverse electrochemical surface finishing process that eliminates the need for low conductivity/high viscosity electrolytes with chemical depassivation additions.

In Figure 1 is presented a generalized pulse/pulse reverse waveform. The anodic pulse is tuned (on-time, t_a, and peak voltage, V_a) to enhance mass transport and control current distribution. While a priori determination of the on-times and peak voltages is not currently known, guiding principles based on single pulse transient studies have been presented in more detail previously.[7] Generally speaking, for uniform polishing of a surface, for hydrodynamic boundary layers conforming to the roughness features (i.e. a macroprofile) the anodic on-time should be relatively small. For hydrodynamic boundary layers much larger than the roughness features (i.e. a microprofile) the anodic on-time should be relatively large. Furthermore, for oxide forming or passive materials, anodic only pulses lead to a rougher surface due to the non-uniform breakthrough of the passive film.[8,9]

In order to depassivate the surface, we intersperse cathodic pulses (on-time, t_c, and peak voltage, V_c) within the anodic pulses, in place of or in conjunction with off-times, t_{off}.[10–13] The off-times are generally inserted between the anodic and cathodic pulses to facilitate replenishment of reacting species and removal of by-products and heat. The cathodic pulse eliminates the need for HF and/or fluoride salts or other chemicals to remove the surface oxide. While the exact mechanism of depassivation is unknown at this stage, we speculate that the cathodic pulses remove the oxide film either by direct electrochemical reduction or indirect chemical reduction, and restore the virgin metal surface prior to the next anodic pulse. The amplitude of the cathodic pulses required for depassivation is material specific, and appears to be based on the strength of the passive film. For metals with stronger oxide films, such as niobium, higher cathodic amplitudes are required (9 to 35 V in this study). Some have suggested using non-aqueous or low water content electrolytes to remove the source of oxygen leading to the formation of the passive film.[14,15] However, from an industrial implementation perspective, these processes are difficult to control, due to the hydroscopic nature of the non-aqueous electrolyte.

The inclusion of cathodic pulses and off-times in the waveform suggests that the overall process would be much slower than a conventional DC process, which is undesirable for industrial implementation. However, the maximum instantaneous current density available during the anodic pulse is higher than the DC limiting current density. Specifically, the ratio between the limiting current density realized in the pulsed electropolishing process, i_p, versus that in steady state, i_{lim}, is:

$$i_p/i_{lim} = [\delta_p/\delta(1 - \gamma_a) + \gamma_a]^{-1} \quad [3]$$

where δ_p is the pulsating diffusion layer thickness, δ is the steady state (DC) boundary layer thickness, and γ_a is the anodic duty cycle, or the

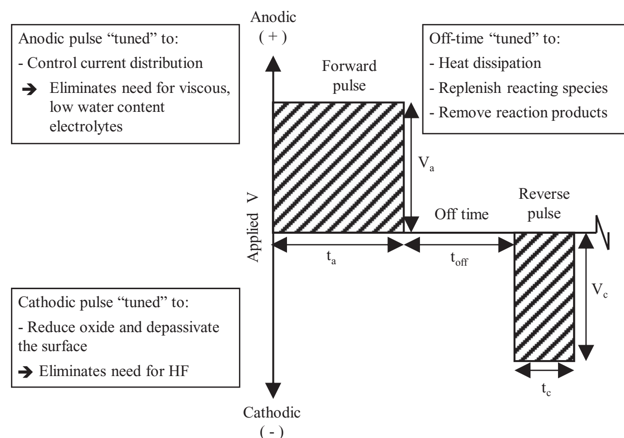

Figure 1. Generalized pulse/pulse reverse waveform for surface finishing of passive materials.

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ratio of the anodic pulse and the total period of the waveform. Ibl and colleagues[16–18] discussed a "duplex diffusion layer" consisting of an inner pulsating layer and an outer stationary layer. Modeling work by Landolt also suggested the existence of a pulsating diffusion layer.[19] 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:[17]

$$\delta_p = (2Dt_{on})^{1/2} \quad [4]$$

where D is the diffusion coefficient and t_{on} is the pulse length. When the pulse on time is equal to the transition time (τ), the concentration of reacting species at the interface drops to zero precisely at the end of the pulse. An expression for τ is provided in the following equation:

$$\tau = ((nF)^2 C_b{}^2 D)/2i_p{}^2 \quad [5]$$

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

$$\delta_p = 2((Dt_{on}/\pi)^{1/2} \quad [6]$$

$$\tau = \pi((nF)^2 C_b{}^2 D)/4i_p{}^2 \quad [7]$$

More recently, Yin[20] using a similar approach as Ibl, derived the same equation for the pulsating diffusion layer for "pulse-with-reverse" electrochemical processes.

Per equation 3, since δ_p must be smaller than δ, higher instantaneous limiting current densities can be achieved in pulsed processes. The extent of this increase is based on the δ_p/δ ratio, which is directly influenced by the anodic pulse on time. A higher limiting current density relates directly to a higher instantaneous metal removal rate. Therefore, the overall removal rate of a pulsed process can rival or exceed that of a DC process despite a duty cycle that is less than 100%, while enjoying enhanced process performance. The waveform is designed such that the anodic pulse compensates for off-times and cathodic pulses such that the average material removal rate (net anodic current density) is equivalent to or greater than DC electropolishing.

In summary, while conventional electropolishing uses a high viscosity electrolyte to focus the current distribution under mass transport, and HF to remove the oxide film, pulse reverse electropolishing is based on non-viscous water electrolytes and 1) uses the anodic pulse time and amplitude to focus the current distribution (without the need for a viscous solution) by qualitatively considering the effect of pulse anodic on-time to pulsating boundary layer thickness and the pulse amplitude on the transition time, 2) uses a cathodic pulse to remove the oxide film and eliminate the need for HF, and 3) uses an off-time to dissipate heat.

We previously reported on the use of pulse (anodic only) electrochemical deburring of 1010 steel automotive planetary gears and pulse reverse electropolishing of stainless steel semiconductor valves in aqueous sodium chloride/sodium nitrate (~15% wt).[21] This paper demonstrates the utility of the pulse reverse approach, as it pertains to electropolishing of niobium. Niobium is used to fabricate superconducting radio frequency (SRF) cavities used for high energy particle accelerators, such as the proposed International Linear Collider. To take full advantage of the superconducting properties of the niobium SRF cavities, the inner surface must be polished to a microscale roughness. While conventional DC electropolishing of niobium is conducted in a viscous electrolyte consisting of nine parts sulfuric acid (96%) to one part hydrofluoric acid (48%),[5,22] this paper focuses on pulse/pulse reverse electropolishing of niobium in a low concentration aqueous sulfuric acid electrolyte.

Experimental

Niobium coupons were obtained from the DOE Fermi National Accelerator Laboratory for electropolishing studies. The coupons were either 25 × 25 mm or 75 × 75 mm, with an initial Ra as high as 1.3 μm, and were electropolished in a flow cell described previously.[23] This is a two-electrode system, as reference electrodes are not conducive to industrial implementation. The anode is the niobium substrate and the cathode is fabricated from mixed metal oxide-coated titanium (WaterStar, Inc., Newbury, OH), an electrode with a low overvoltage and a long history of durability in aggressive environments. The electropolishing solution was 5 to 50 wt% aqueous H_2SO_4. Surface roughness measurements were measured using a stylus profilometry over a distance of 12 mm or using Atomic Force Microscopy at the DOE Thomas Jefferson National Accelerator Facility. The pulse reverse rectifiers used were from Dynatronix, Inc. Herein we report the results for electropolishing of niobium coupons using three pulse reverse waveforms as tabulated in Table I, 1) high frequency/high power waveform, 2) low frequency/ low power waveform, and 3) low frequency/very low power waveform.

Table I. Pulse reverse waveform parameters used for electropolishing of niobium coupons.

Waveform	V_{anodic} (V)	t_{anodic} (ms)	t_{off} (ms)	$V_{cathodic}$ (V)	$t_{cathodic}$ (ms)
High frequency High power	30	0.06	5.0	35	0.20
Low frequency Low power	3	2.50	1.0	9	2.50
Low frequency Very low power	0	2.50	2.5	15	2.50

Results and Discussion

High frequency/high power waveform.— We processed niobium coupons in 30 wt% H_2SO_4 using the high frequency/high power waveform presented in Table I. Based on the guidance above, this waveform employs a high anodic peak voltage of 35 V for an anodic on-time of 0.06 ms, followed by an off-time of 5 ms, to allow removal of heat built up during polishing. Finally, a cathodic voltage of 35 V is applied for 0.2 ms. The relatively short anodic and cathodic on-times enable the use of high peak voltages and maintain mass transport control and uniform processing during oxide film formation (anodic) and removal (cathodic). The electropolished surface (Fig. 2) exhibited a mirror like finish and the R_a measured using a Mitutoyo SJ-400 stylus profilometer was ~0.05 μm, which is at the minimum detection limit of this measurement tool. A sample was provided to the DOE

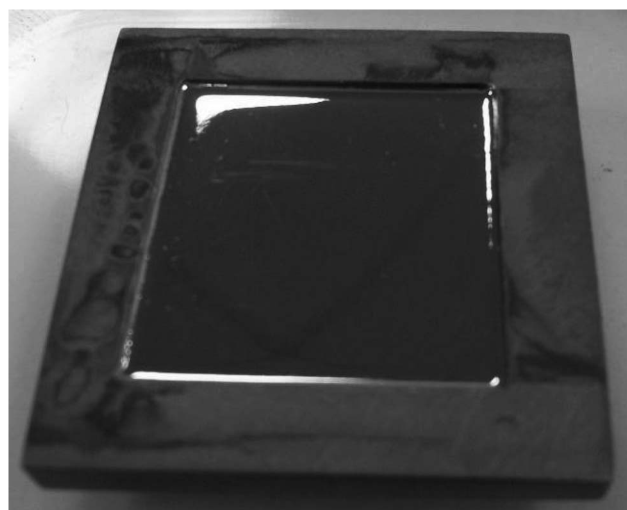

Figure 2. Niobium coupon electropolished using the high frequency/high power waveform from Table I: $V_{anodic} = 30$ V, $t_{anodic} = 0.06$ ms, $t_{off} = 5.0$ ms, $V_{cathodic} = 35$ V, $t_{cathodic} = 0.20$ ms, in an electrolyte of 30 wt% H_2SO_4. The edge of the coupon shows the surface finish prior to polishing. The polished surface R_a ~0.05 μm.

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Table II. Surface roughness of the niobium coupon electropolished using the high frequency/high power waveform from Table I: V_{anodic} = 30 V, t_{anodic} = 0.06 ms, t_{off} = 5.0 ms, $V_{cathodic}$ = 35 V, $t_{cathodic}$ = 0.20 ms, in an electrolyte of 30 wt% H_2SO_4, measured using Atomic Force Microscopy.

Scan Size (μm)	R_{max} (nm)	R_a (nm)	RMS (nm)
50 × 50	47.3	3.3	4.3
10 × 10	19.4	1.3	1.7
2 × 2	9.4	0.4	0.5

Thomas Jefferson National Accelerator Facility for surface analysis by scanning electron microscopy and surface roughness measurement using atomic force microscopy. Up to three scans were conducted and the averages are presented in Table II. Surface roughness values below 1 nm were measured over small regions of electropolished surface. (Note, such detailed measurements over very small areas are standard practice for surface evaluation at the Thomas Jefferson National Accelerator Facility). The surface cleanliness and roughness were comparable to that obtained using standard electropolishing (9 parts H_2SO_4 (96%) to 1 part HF (49%).[24]

Amelioration of heat buildup.— We investigated the utility of the off-time in the applied waveform to ameliorate the buildup of heat during electropolishing in 30% H_2SO_4 using the high frequency/high power waveform presented in Table I. Heat buildup in the electrolyte during electropolishing is considered undesirable for the performance of SRF cavities. The niobium coupon size was 75 × 75 mm and the electropolishing cell contained 15 L of electrolyte. The off-time was varied from 0.3 to 5.0 ms and the temperature was measured at the beginning and end of electropolishing. The data are presented in Table III. For an off-time of 0.3 ms, after 40 minutes of electropolishing we observed significant heat buildup from 15 to 33°C. When the off-time was increased to 0.6 ms, the heat buildup remained approximately the same even for a 120 minute processing time. Increasing the off-time to 1.0 ms, we observed reduced heat buildup for 120 minute processing time. Finally, with a 5.0 ms off-time, we observed minimal heat buildup even for a processing time of 560 minutes.

Low frequency/low power waveform.— In order to scale-up the niobium electropolishing process to larger devices, such as SRF cavities, we need to consider the frequency/power constraints of commercially available rectifiers. Single-cell and nine-cell SRF cavities have surface areas of 0.123 and 0.86 m^2, respectively, and as such require rectifiers with sufficiently available power to accommodate the total currents drawn during electropolishing. Consequently, we investigated waveforms with lower frequencies and lower voltages that would draw less total current, and enable the use of commercially available rectifiers. After limited development efforts, we settled on the low frequency/low power waveform presented in Table I. This waveform employs an anodic peak voltage of 3 V for an anodic on-time of 2.5 ms. This is followed by an off-time of 1 ms, sufficient to avoid excessive heat buildup during electropolishing of niobium coupons. Finally, a cathodic voltage of 9 V is applied for 2.5 ms. Because these anodic and cathodic on-times are relatively longer than

Table III. Effect of the length of the off-time in the pulse reverse waveform on heat buildup in the electrolyte.

t_{off} (ms)	Total Time (min)	Initial Temperature (°C)	Final Temperature (°C)
0.3	40	15	33
0.6	120	14	35
1.0	120	14	28
5.0	560	16	19

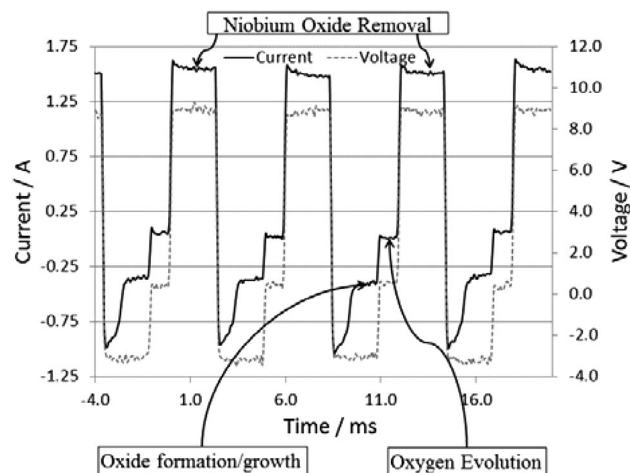

Figure 3. Pulse reverse voltage and current response during electropolishing of flat niobium coupons for the low frequency/low power waveform from Table I: V_{anodic} = 3 V, t_{anodic} = 2.50 ms, t_{off} = 1.0 ms, $V_{cathodic}$ = 9 V, $t_{cathodic}$ = 2.50 ms, in an electrolyte of 15 wt% H_2SO_4.

for the high power/high frequency waveform, the applied voltages must be lower. As polishing is maintained, we believe that we are still under a macroprofile, and therefore the waveform parameters enable mass transport control and uniform processing. Using this low frequency/low power waveform, the surface finish was mirror-like and the R_a, as measured by stylus profilometry, was ~0.05 μm.

As a rule, we always monitor the waveform during processing using an oscilloscope, to ensure that the waveform applied at the anode is the same as that programmed into the rectifier. In Fig. 3, we present the oscilloscope trace of the low frequency/low power electropolishing waveform. The voltage trace indicates excellent agreement between the input voltage parameters: 3 V anodic for 2.5 ms/1.0 msec off-time/9 V cathodic for 2.5 ms.

Cathodic electropolishing.— During the anodic voltage portion of the waveform, we noted an anodic current response that was initially high, and we attribute this peak to niobium oxide formation/growth; some oxygen evolution may also be occurring during this time. The anodic current then transitions to a lower current plateau, which we attribute solely to oxygen evolution. During the off-time, the current response is approximately zero, allowing dissipation of heat in the vicinity of the niobium surface. During the cathodic voltage portion of the waveform, we noted a cathodic current response that we attribute to niobium oxide removal, speculated to be by either a direct electrochemical or an indirect chemical mechanism. While we have found no evidence for direct electrochemical removal of niobium oxide in an aqueous solution, in cyclic voltammetric experiments, a cathodic peak subsequent to niobium oxide formation has been reported; however this peak was attributed to hydrogen insertion into the oxide matrix.[25] It is also likely that hydrogen evolution is occurring during the cathodic peak and contributing to the measured cathodic current response. We do observe gassing at the niobium surface during these experiments.

As noted in the introduction, the use of short on-times allows us to administer high peak voltages and currents. The waveform is typically designed such that the applied anodic current compensates for off-times and cathodic current to achieve a net anodic current density equivalent to or greater than DC electropolishing. Fig. 3 shows that in this case, the portion of the anodic peak voltage and current response that we attribute to niobium oxide formation is considerably smaller than the cathodic peak voltage and current response. As we do get net niobium metal removal (i.e. a net anodic process), this suggests that the majority of the current observed during the cathodic peak may be

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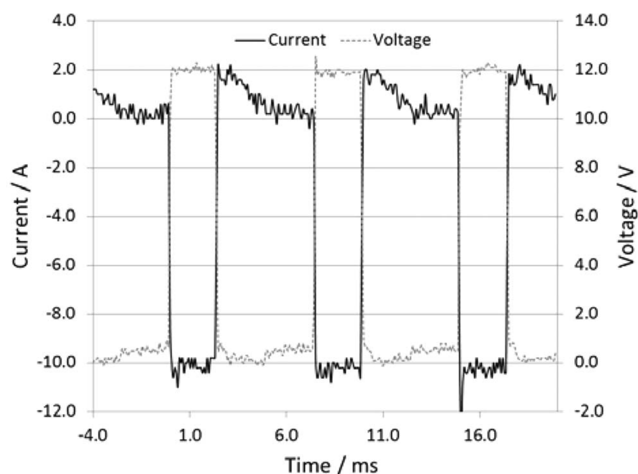

Figure 4. Pulse reverse voltage and current response during electropolishing of flat niobium coupons for the low frequency/very low power waveform from Table I: $V_{anodic} = 0$ V, $t_{anodic} = 2.50$ ms, $t_{off} = 2.5$ ms, $V_{cathodic} = 15$ V, $t_{cathodic} = 2.50$ ms, in an electrolyte of 30 wt% H_2SO_4.

attributable to hydrogen evolution. The respective current efficiencies of the anodic and cathodic processes are unknown at this stage.

In summary, for pulse reverse electropolishing of niobium we speculate that we are anodically forming an oxide film (per Eqn. 2), then cathodically removing that film to effectively consume niobium metal, rather than directly electrochemically oxidizing Nb to Nb^{2+} in solution (per Eqn. 1). This may be termed "cathodic electropolishing", and is a phenomenon that we have only observed with electropolishing of niobium.

To further investigate the phenomenon of cathodic electropolishing, we applied a low frequency / very low power waveform (Table I) that employs an applied anodic peak voltage of 0 V for an anodic on-time of 2.5 ms and an off-time of 2.5 ms (rather than a total off-time of 5.0 ms), followed by a cathodic voltage of 12 V for 2.5 ms. The oscilloscope trace of the applied waveform, Fig. 4, shows that an anodic current response was observed during the applied anodic voltage of 0 V, and we attribute this to oxide formation. During electropolishing, the surface finish of this niobium coupon decreased from 1.10 μm down to 0.40 μm. While not as good a final surface finish as for the other waveforms, electropolishing was observed.

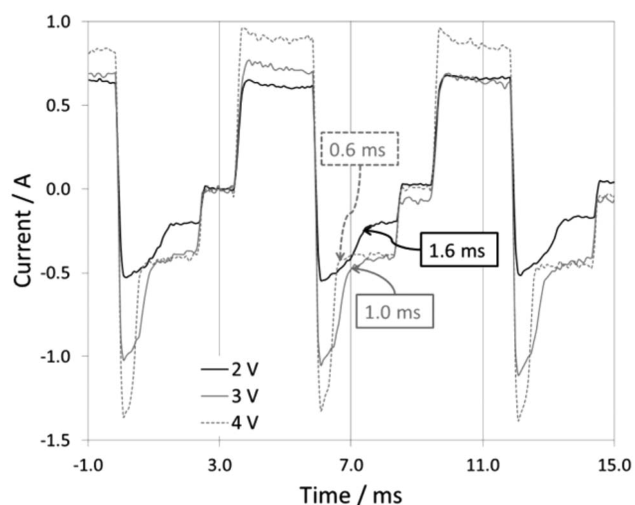

Figure 5. Current response during electropolishing of niobium coupons, in an electrolyte of 15 wt% H_2SO_4, for varying anodic voltages, where the waveform parameters were: $V_{anodic} = 2$, 3 or 4 V, $t_{anodic} = 2.50$ ms, $t_{off} = 1.0$ ms, $V_{cathodic} = 6$ V, $t_{cathodic} = 2.50$ ms. The chart identifies a decrease in the anodic current transition time with increasing anodic voltage.

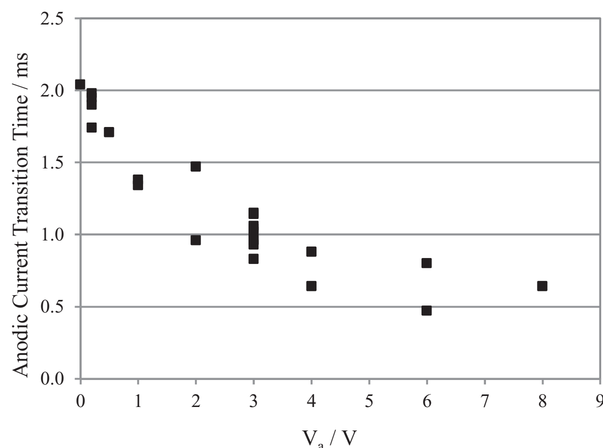

Figure 6. Decrease in anodic current transition time as a function of applied anodic peak voltage for electropolishing of niobium coupons in a 15 to 50 wt% H_2SO_4 electrolyte.

Anodic current transition.— In order to further investigate the nature of the anodic current transition from oxide film formation to oxide evolution, we varied the anodic voltage from 2 V to 4 V, while maintaining all other parameters for the low frequency/low power waveform. Fig. 5 shows that as the anodic voltage is increased, the time for the transition from the high current to low current plateau decreases from ~1.6 ms to ~0.6 ms. Fig. 6 shows the relationship between the anodic current transition time and anodic peak voltage, over a voltage range of 0.2 to 8 V. Note, these tests were run in H_2SO_4 concentrations ranging from 15 to 50 wt%, and there does not appear to be a strong effect of H_2SO_4 concentration on the anodic current transition time in this preliminary study. We speculate that the observed high current to low current plateau transition is due to the transition from niobium oxide formation to oxygen evolution.

In recent experiments, we note that the high current to low current plateau transition time strongly correlates with effective electropolishing of niobium coupons, i.e. R_a values less than 0.1 μm. Based on this observation, we control the current plateau transition time by adjusting the pulse reverse waveform parameters to account for 1) different distances from the cathode tool to the niobium coupon, and 2) different area ratios of cathode tool to niobium surface. These correlations are important for adapting the coupon work to the electropolishing of actual niobium SRF cavities where the cathode to niobium surface distance varies from ~1 to 3.5" and the cathode tool surface area to niobium surface varies from ~1:2 to 1:5.

Conclusions

The mechanistic aspects of conventional DC electropolishing have long been understood to involve diffusion limited access[4] to the metal surface of interest involving, for example either diffusion of the metal ion away from the surface[26] or diffusion of an acceptor ion to the surface.[27] For microprofile leveling, the use of viscous electrolytes with a large boundary layer was suggested. In the case of niobium, the electropolishing mechanism is based on diffusion limited access of fluoride ion to the niobium surface.[5,22]

While the mechanistic aspects of pulse reverse electropolishing of niobium are not understood, they are clearly distinct to those of conventional electropolishing in that our electrolyte contains 50 to 95% water and is low viscosity. In addition, our pulse reverse process does not contain hydrofluoric acid, added to remove the surface oxide during conventional DC electropolishing. We speculate that we are anodically forming an oxide film, then cathodically removing

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that film to effectively consume niobium metal, rather than directly electrochemically oxidizing Nb to Nb^{2+} in solution.

We note a transition in the anodic current response from a high current to a lower current plateau. The time for this transition is inversely related to the anodic pulse potential. We speculate that the current response profile is attributed to the transition from niobium oxide formation to oxygen evolution on the oxide covered surface. While additional work is required to elucidate the mechanistic aspects of pulse reverse electropolishing in low viscosity aqueous electrolytes, we have observed that the presence of the anodic current transition is important to effectively electropolish niobium at different cathode to niobium surface separations and different cathode to niobium surface area ratios. Finally, our efforts are directed toward developing a commercial based process and was based on a two electrode cell. More insight into the mechanistic aspects of the pulse reverse electropolishing of niobium may be possible with three electrode studies.

In summary, we have described a pulse reverse electropolishing process using low viscosity aqueous electrolytes, devoid of aggressive chemicals for depassivating the surface. Consequently, the safety and chemical handling and disposal issues associated with the pulse reverse electropolishing process are minimized. In addition, the need for active chilling is minimized by the appropriate use of the off-time and we anticipate that the electropolishing process reproducibility and robustness are greatly enhanced. In on-going work,we are applying the pulse reverse electropolishing process to single-cell SRF niobium cavities for superconducting performance evaluation at the DOE Fermi National Accelerator Laboratory. In addition, the pulse reverse electropolishing approach described herein should be applicable to other materials, such as valve metals, thereby eliminating the need for aggressive concentrated HF-containing electrolytes.

Acknowledgments

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