ELECTROPOLISHING OF NIOBIUM SRF CAVITIES IN LOW VISCOSITY AQUEOUS ELECTROLYTES WITHOUT HYDROFLUORIC ACID*

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Abstract

Electropolishing of niobium materials and cavities is conventionally conducted in high viscosity electrolytes consisting of concentrated sulfuric and hydrofluoric acids. The use of these dangerous and ecologically damaging chemicals requires careful attention to safety protocol to avoid harmful worker exposure and environmental damage. We present an approach based on pulse reverse waveforms enabling the use of low viscosity water based electrolytes without hydrofluoric acid for electropolishing of niobium materials. The subtleties of the bipolar electropolishing process vis-a-vis conventional electropolishing are presented.

INTRODUCTION

Electropolishing (EP) is used for final surface finishing of niobium SRF cavities to achieve acceptable performance. EP is a surface finishing process whereby surface asperities are preferentially removed by anodic electrolytic dissolution under the influence of a direct current (DC) electric field in an appropriate electrolyte. Conventional EP processing for niobium cavities is based on a viscous electrolyte consisting of a mixture of sulphuric acid (95-98%) and hydrofluoric acid (49%) in a 9:1 volume ratio [1]. The need for a viscous electrolyte for effective EP is mechanistically understood in terms of the "viscous salt film theory" proposed by Jacquet [2] and is generally applicable to all metal-electrolyte systems [3] Hydrofluoric acid is added to completely remove the oxide film from the surface [4]. A recent study of niobium EP reports diffusion limited access of fluoride ion to the surface and is generally consistent with the viscous salt film theory [5]. In collaboration with Fermi National Accelerator Laboratory (Fermilab), we are addressing the need for an eco-friendly EP process.

TECHNICAL APPROACH

In contrast to EP using DC electric fields, our approach is based on pulse reverse pulse waveforms (i.e. bipolar EP). In Figure 1 is presented a generalized pulse reverse waveform. The anodic pulse is tuned to enhance mass transport, control current distribution and focus the current on the asperities and eliminate the need for a high viscosity electrolyte. To depassivate the surface, we intersperse cathodic pulses within the anodic pulses, in place of or in conjunction with off-times [6-9]. The off-times are generally inserted between the anodic and cathodic pulses to facilitate replenishment of reacting
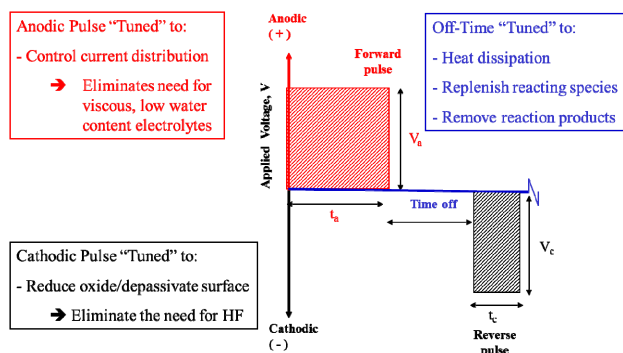
Figure 1: Generalized pulse reverse waveform for surface finishing of passive materials.

species, and removal of by-products and heat. The cathodic pulse eliminates the need for hydrofluoric acid to remove the surface oxide. The exact mechanism of depassivation is unknown at this stage. The amplitude of the cathodic pulses required for depassivation is material specific and appears to be based on the strength of the passive film. 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 [10].

EXPERIMENTAL

Fermilab provided four single-cell niobium SRF cavities for bipolar EP studies. The initial cavity was used to transition from coupons and develop the process parameters for cavities. The remaining cavities were processed conventionally and provided a baseline for comparison after bipolar EP. Since the emphasis of the current project is to demonstrate the ability to develop an eco-friendly process for cavity electropolishing, minimal effort was directed towards the development and optimization of pulse reverse waveform parameters. After initial experiments with a "developmental" cavity, subsequent cavity trials used processing conditions:

1) 5 wt% H_2SO_4 in water; 4 V anodic for 200 ms followed by off for 300 msec followed by 10 V cathodic for 200 ms, and/or
2) 10 wt% H_2SO_4 in water; 4 V anodic for 100 ms followed by off for 150 msec followed by 10 V cathodic for 100 ms.

RESULTS AND DISCUSSION

We previously reported results on the application of pulse reverse electropolishing of niobium coupons in 5 to 50 wt% H_2SO_4 in water [11]. In the prior work, we reported a current transient in the anodic current which we attributed to a transition from oxide film

formation/growth followed by oxygen evolution. We speculated that our polishing mechanism occurred by removal of the niobium oxide during the cathodic pulse and termed this process termed "cathodic electropolishing."

We observed that the presence of the anodic current transition is important to effectively electropolish niobium. To adapt bipolar EP to single-cell cavities, we adjusted the timing of the waveforms to provide sufficient time for the anodic current transition. In a single-cell SRF cavity, the gap from the cathode to the niobium surface and the area ratio of the cathode to the niobium surface vary from ~1 to 3.5" and ~1:2 to 1:5, respectively. We conducted electropolishing of coupons at separations and area ratios representative of these parameters and observed 1) as the coupon gap increases the waveform frequency decreases, and 2) as the coupon surface area ratio increases the waveform frequency decreases.

In initial experiments, the "development" cavity (TE1NR001) was processed in an apparatus constructed at Faraday based on the design specifications of Argonne National Laboratory/Fermilab [12]. The cavities were processed in a horizontal orientation with ~60% of the internal volume filled with 5 wt% H_2SO_4 in water electrolyte and rotated at 1 rpm. After a number of unsuccessful trials based on visual observations, we revisited the original Siemens literature [13] upon which current cavity processing is derived [1] with advancements by KEK [14] and others. The current cavity electropolishing protocol (horizontal orientation, partial electrolyte fill, rotation) were developed for the highly viscous sulfuric/hydrofluoric acid solution in order to avoid undesired streaking due to bubbles and generate an appropriate "electrolyte film" during cavity rotation. Since the viscosity of our low concentration sulfuric acid solution is much less than that of the sulfuric/hydrofluoric acid solution, we speculated that horizontal operation with partial cavity fill and rotation may not be required or desirable for the bipolar EP process [15].

Additional electropolishing experiments were conducted in 5 wt% H_2SO_4 in water with the cavity in a vertical orientation completely filled with electrolyte and without rotation. Visual inspection at Faraday indicated acceptable electropolishing and was confirmed at Fermilab [16]. All subsequent processing trials were conducted with the cavity in a vertical orientation, filled with electrolyte and without rotation.

Performance Experiment #1 consisted of "light EP" on cavity (TE1DESYB5) in 5 wt% H_2SO_4 in water (4 V anodic for 200 ms: off for 300 msec: 10 V cathodic for 200 ms) with an average over the RF surface of ~30 μm of material removed as measured with an ultrasonic thickness gauge. The cavity performed with a quench field about 31 MV/m with a low-field Q_0 of 2.0E+10 which is within the normal performance band of a cavity receiving standard EP [16].

Performance Experiment #2 consisted of "heavy EP" on cavity (TE1AES007) in 5 wt% H_2SO_4 in water (4 V anodic for 200 ms: off for 300 msec: 10 V cathodic for 200 ms) with ~15 μm material removed followed by additional processing in 10 wt% H_2SO_4 in water (4 V anodic for 100 ms: off for 150 msec: 10 V cathodic for 100 ms) with ~70 μm average material removed (Total material removal for this cavity was ~100 μm as measured by ultrasonic thickness gauge). The cavity exhibited "average" performance as well as Q-disease, which was eliminated after bake. This behavior is consistent with bulk removal using the current practice [16].

Performance experiment #3 consisted of "light EP" on the same cavity (TE1AES007) to demonstrate that the bipolar pulse process did not cause Q-disease for small material removal. The cavity was processed in 10 wt% H_2SO_4 in water (4 V anodic for 100 ms: off for 150 msec: 10 V cathodic for 100 ms) with ~~20 μm material removed at the equator. The cavity was evaluated at Fermilab and did not exhibit Q-disease [16].

Performance Experiment #4 consisted of "light EP" on a "high performing" cavity (TE1AES012) in 10 wt% H_2SO_4 in water (4 V anodic for 100 ms: off for 150 msec: 10 V cathodic for 100 ms) with ~25 μm average of material removed. The cavity achieved a maximum gradient of ~44MV/m with a Q of $1x10^{10}$, the highest gradient and Q value at this gradient observed at Fermilab in any cavity regardless of processing technique [16].

Minimal pulse reverse waveform optimization and activities directed towards mechanistic understanding were conducted in this program. More extensive waveform optimization and mechanistic understanding could lead to the development of 1) a pulse reverse waveform enabling neutral salt electropolishing electrolyte, and/or 2) a pulse reverse waveform for bulk removal that would sequence with the final electropolishing waveform to form a one-step, seamless surface finishing process. As an example, in the case of stainless steel semiconductor valve electropolishing, we conducted both bulk material removal and final electropolishing by sequentially applying a "bulk removal waveform" followed by a "final electropolishing waveform" in the same sodium chloride electrolyte in the same apparatus in one process step [9]. Additionally, in our limited coupon studies on niobium we have observed material removal rates of up to 5 μm/min, which would be enabling for rapid bulk removal in SRF cavities [12].

Bipolar EP was deployed with a vertical cavity orientation completely filled with electrolyte and without rotation. The benefits of vertical electropolishing has been noted and includes elimination of rotary acid seals, sliding electrical contacts, and vertical/horizontal control fixtures, and simplifies plumbing and containment leading to lower capital costs, enabling multiple cavities to be processed simultaneously [17]. Based on the potential for sequenced pulse reverse waveforms for bulk removal and final electropolishing we envision an industrially compatible process shown in Figure 2, analogous to electroplating of internal components. Multiple SRF cavities are arranged to include multiple fluid deliveries and exit gas manifolds. The cavities could be sprayed or submerged in a
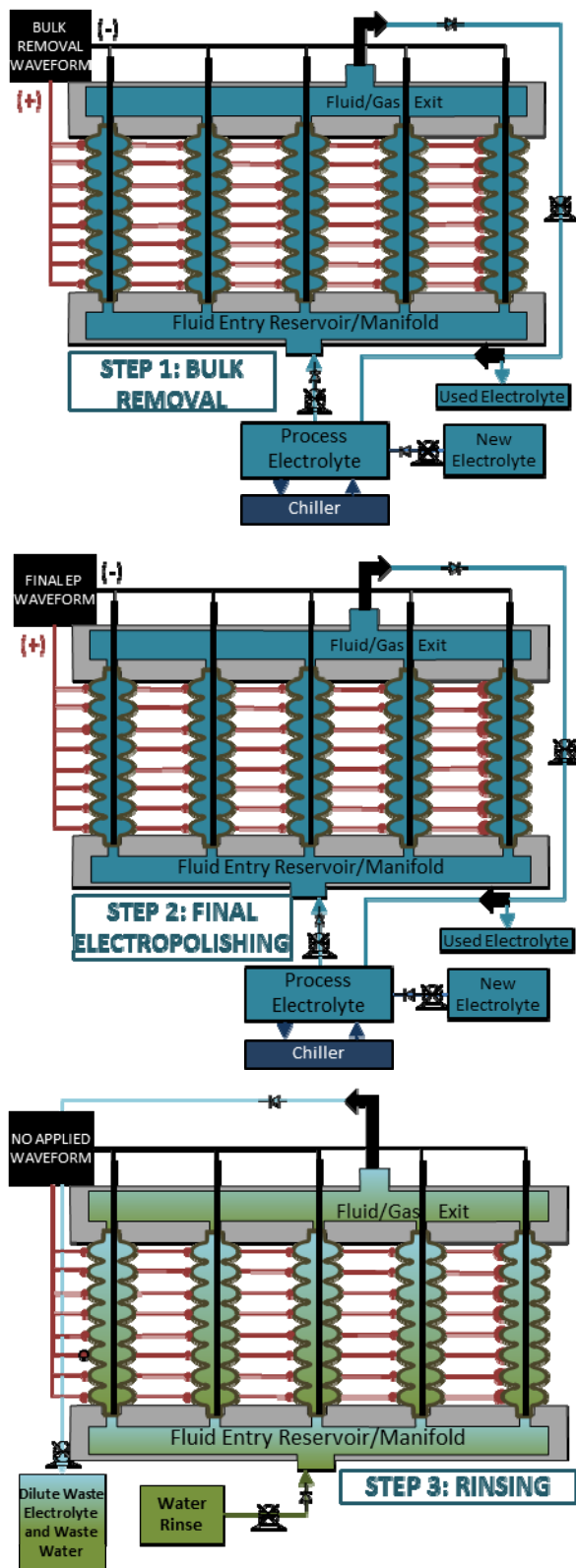
Figure 2: Conceptual implementation of bipolar EP.

other change in the equipment configuration or electrolyte. During Step 3, ultrasonic detergent cleaning and ultra-pure water rinsing is accomplished. At this point, the cavities could be removed for high pressure water rinsing and drying operations, as required, or those processes could be brought to the cavities. The transition from the bulk removal waveform to the final electropolishing waveform is accomplished by sequencing pulse reverse waveforms in the rectifier control system in the same electrolyte and in a single apparatus, offering considerable industrial throughput and cost advantages.

SUMMARY

We report on recent development activities directed towards an "eco-friendly" electropolishing process for niobium SRF cavities. Bipolar EP uses an aqueous sulphuric acid electrolyte without the addition of hydrofluoric acid. With minimal optimization of pulse reverse waveform parameters we have demonstrated the ability to electropolish single-cell niobium SRF cavities and achieve at least equivalent performance compared to conventionally processed cavities. The pulse reverse waveform process suggests a new paradigm in contrast to the ~80 year understanding that electropolishing can only occur in low viscosity electrolytes under mass transport control. While additional work is required to elucidate the mechanistic aspects of the pulse reverse process we tentatively refer to this process as "cathodic electropolishing."

In addition to the "eco-friendly" nature of bipolar EP, we electropolished cavities in a vertical orientation, filled with electrolyte and without rotation. Consequently, Bipolar EP offers numerous advantages from an industrial processing perspective. We speculate that waveforms could be developed for bulk material removal as well as employing neutral salt electrolytes. Finally, developments in cavity processing such as shielding, external cooling and high surface area cathodes are adaptable to the bipolar EP process.

temperature controlled "cooling" solution or in the electropolishing electrolyte. In Step 1, a pulse reverse waveform tuned for bulk removal is applied to the cavity. During Step 2, a pulse reverse waveform tuned to accomplish final electropolishing is applied, without any

REFERENCES

[1] F. Eozenou, A. Aspart, C. Antoine, B. Malki CARE Report 06-10-SRF, EU contract number RII3-CT-2003-506396 (2006).

[2] P.A. Jacquet Trans. Electrochem. Soc. 69, 629 (1936).

[3] D. Landolt Electrochimica Acta 42, 1-11, (1987).

[4] B. MacDougal in High Metal Dissolution Processes eds. M. Datta, B. MacDougal, J. Fenton PV 95-19, The Electrochemical Society, Pennington, NJ (1996).

[5] H. Tian, S. Corcoran, C. Reece, M. Kelly J. Electrochem. Soc. 155 D563-8 (2008).

[6] J. Sun, E.J. Taylor, R. Srinivasan, J. Materials Processing Technology, 108(3), 356 (2001).

[7] C. Zhou, E.J. Taylor, J. Sun, L. Gebhart, R. Renz, U.S. Patent No. 6,402,931, 6-11-02.

[8] M. Inman, E.J. Taylor, A. Lozano-Morales, T. Hall, H. Garich, U.S. Patent Appl. No. 13/153,874 6-11-10.

[9] E.J. Taylor, U.S. Patent No. 6,558,231 5-6-03.

[10] E.J. Taylor, J. Appl. Sur. Fin., 3 (4), 178 (2008); Plating & Surface Finishing, 95 (12), 24 (2008).

[11] M. Inman, E.J. Taylor, T. Hall J. Electrochem. Soc. 160 E94-E98 (2013).

[12] M. Inman, H. Garich, S. Snyder, E.J. Taylor, L. Cooley, C.A. Cooper, A. Rowe SRF2011-TUPO017 (2011).

[13] H. Diepers, O. Schmidt U.S. Patent No. 3,939,053 2-17-72.

[14] K. Saito, Y. Kojima, T. Furuya, S. Mitsunobu, S. Noguchi, K. Hosoyama, T. Nakazato, T. Tajima, K. Asano, K. Inoue Proceeding 4th SRF Workshop, Vol. 2, KEK, Tsukuba, Japan (1989).

[15] E.J. Taylor, M. Inman, T. Hall U.S. Patent Application No. 13/546,072 filed 7-11-12.

[16] A. Rowe, A, Grassellino, T. Hall, M. Inman, S. Snyder, E.J. Taylor SRF2013-TUIC02 (2013).

[17] F. Furuta, G. Hoffstaetter, M. Ge, M. Liepe, B. Elmore, C. Crawford IPAC2012 TUPPR045 (2012).