ELECTROPOLISHING OF NIOBIUM SRF CAVITIES IN ECO-FRIENDLY AQUEOUS ELECTROLYTES WITHOUT HYDROFLUORIC ACID

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ABSTRACT

Electropolishing of niobium cavities is conventionally conducted in high viscosity electrolytes consisting of concentrated sulfuric and hydrofluoric acids. The use of dangerous and ecologically damaging chemicals requires careful attention to safety protocols to avoid harmful worker exposure and environmental damage. We present an approach for electropolishing of niobium materials based on pulse reverse waveforms, enabling the use of low viscosity aqueous dilute sulfuric acid electrolytes without hydrofluoric acid, or aqueous near-neutral pH salt solutions without any acid. Results will be summarized for both cavity and coupon electropolishing for bulk and final polishing steps. 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. Cavities are electropolished in a vertical orientation filled with electrolyte and without rotation, offering numerous advantages from an industrial processing perspective. Shielding, external cooling and high surface area cathodes are adaptable to the bipolar EP process.

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 for SRF 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 completely removes the oxide 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) and Cornell University, 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). Fig. 1 presents a generalized pulse reverse waveform. The anodic pulse is tuned to enhance mass transport, control current distribution, 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 [6,7,8,9]. 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 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 previously [10].
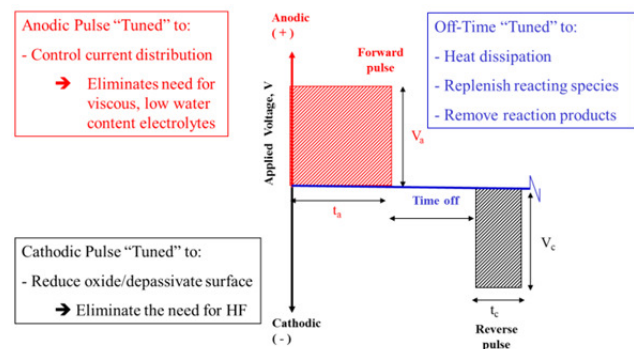

Figure 1: Generalized pulse reverse waveform for surface finishing of passive materials.

We have reported on the application of pulse reverse electropolishing of niobium coupons in 5 to 50 wt% H_2SO_4 in water [11]. We observed a current transient in the anodic current that we attributed to a transition from oxide film formation/growth to 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. We applied the process to the final electropolishing step for single-cell SRF cavities provided by Fermilab, and Fermilab testing showed RF performance characteristics very similar to those achieved using conventional hydrofluoric acid-based processing. Bipolar EP achieved accelerating gradients above 40 MV/m and Q_0 above 1E+10 at 35 MV/m using an electrolyte "*no more hazardous or ecologically unfriendly than a household cleaner*" [12,13].

Discussions with Fermilab suggested two further avenues for exploration: 1) increase of the material removal rate so as to apply the process to the bulk electropolishing step, and 2) adaptation of this process to fully acid-free electrolytes, so as to further improve worker health and safety, and reduce cost. These aspects are the focus of current projects with Cornell University.

BULK BIPOLAR EP IN DILUTE SULFURIC ACID

This DOE SBIR program is directed towards increasing the removal rates of the Bipolar EP process, so as to enable a bulk Bipolar EP process step during cavity fabrication. In coupon studies, we optimized Bipolar EP process parameters to achieve niobium removal rates that are compatible with bulk processing, while maintaining surface finishes specified by FNAL. We simulated anode to cathode gaps and area ratios inside the cavity using coupons and tested Bipolar EP in a 10 w/w% H_2SO_4 electrolyte. The Nb removal rate for a specific waveform did not appear to vary with a change in gap or electrolyte flow rate. The Nb removal rate seemed to be consistently higher (~12%) when the temperature was <21°C. The Nb removal rate increased with waveform frequency, and we observed a max. removal rate of ~0.2 µm/min. The data suggests that the processing conditions are capable of successfully removing material without damaging the Nb surface. The lowest final average Ra achieved in Phase I was 0.26 µm, although the focus of development was more on the removal rate and not on the final surface roughness.

We transitioned Bipolar EP to single-cell cavity processing, and improved Nb removal rates from 0.03 (prior work) to 0.13-0.14 µm/min, more than 4x the rates achieved in prior work, while maintaining the electrolyte temperature below 25°C. While these rates were ~2x less than the 0.3 µm/min achieved by AES using the conventional HF acid-based process, the extremely low capital and operating costs of Bipolar EP are such that we can build inexpensive facilities to maintain the required cavity processing throughput for the ILC[14].

We anticipate that lower operating temperatures would be obtainable with larger capacity refrigeration units and/or different part fixturing, which may further accelerate the removal rate. The average Nb thickness removed from the cavity was measured by Fermilab as ~51 µm, considered sufficient to demonstrate the efficacy

of the technology. The beam tubes had a higher removal rate than the equator; as is commonly observed in convention sulfuric/hydrofluoric acid EP. We anticipate the non-uniform current distribution (i.e. non-uniform material removal) can be overcome with shields and/or masked electrodes similar to other electrochemical process designs. Fermilab tested the cavity prior to hydrogen bake out and exhibited Q disease. We speculate this is due to the higher cathodic voltages used in this study. Upon baking/ reprocessing, cavity performance was recovered.

ACID-FREE FINAL BIPOLAR EP

This DOE SBIR program is directed towards adapting the Bipolar EP process for near-neutral aqueous salt electrolytes, without any acid, for the final electropolishing step during cavity fabrication. Faraday has demonstrated the feasibility of near-neutral aqueous salt electrolytes for Nb electropolishing in coupon studies. Target performance criteria were evaluated via final Ra, surface appearance and material removal rate. After trials with a wide range of potential electrolytes, a KCl baseline electrolyte was selected owing to its ability to polish coupons to a desired finish and below-target Ra (0.2 µm) values, as well as comparatively high material removal rates. Gradual pH increase during electropolishing in this baseline solution was successfully prevented by incorporation of monobasic potassium phosphate in low concentrations, which also inhibited the deposition of particles on the cathode surface.

Ra values as low as 0.05 µm in combination with bright surfaces with metallic appearance were obtained on 2.5 x 2.5 x 0.32 cm flat coupons. This was significantly below the target Ra, and led to the transition to larger substrates, e. g. 7.6 x 7.6 x 0.32 cm (Fig. 2). Ra values as low as 0.17 µm were measured on the larger coupons and the rate of material removal was ~42 µm/hr.
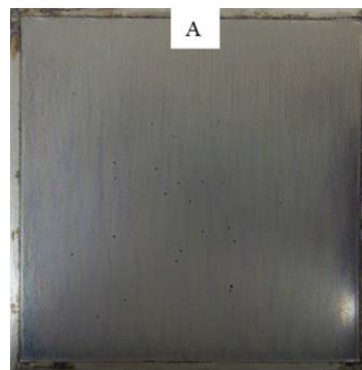

Figure 2: Nb (7.6 cm x 7.6 cm) electropolished in KCl/KH_2PO_4 (200/3 g/L).

The transition from flat coupons to single-cell cavity processing required additional trials with the larger coupons to simulate a SRF cavity processing environment. The cavity anode-to-cathode gap and area ratios was simulated and trials indicated that the anode to

cathode gap did not have a large effect on Ra, appearance and removal rate within the range required for SRF cavity processing, while high surface area cathodes may give better current distribution uniformity and Ra values than traditional rod or tube cathodes.

Due to scheduling difficulties, we were unable to get the cavities tested, and we anticipate single- and multi-cell cavity testing in ongoing project work.

ECONOMIC ANALYSIS SUMMARY

Based on a first order economic analysis, done in conjunction with AES, we concluded that FARADAYIC® Bipolar EP offers substantial savings relative to Baseline EP in terms of operating, capital and intangible. In terms of tangible savings, the cost per cavity for Bipolar EP and Baseline EP are $1,293 and $4,828 per cavity, respectively. The continued development and validation of the Bipolar EP process on multi-cell cavities will contribute greatly to the industrialization of SRF accelerator technology [14].

VERTICAL ELECTROPOLISHING APPARATUS DEVELOPMENT

During the early developmental work on Bipolar EP, Faraday recreated a tooling and fixturing design from Argonne National Laboratory that was designed for conventional processing in the horizontal orientation. However, during the research we learned that a strong feature of Faraday's Bipolar EP technology is the ability to utilize a vertical cavity orientation, completely filled with electrolyte and without rotation. The benefits of vertical electropolishing includes elimination of rotary acid seals, sliding electrical contacts, and vertical/horizontal control fixtures, and simplifies plumbing and containment leading to lower capital costs, and enabling multiple cavities to be processed simultaneously [15]. If vertical bipolar EP is as effective at processing multi-cell cavities, the scalability, throughput rates and reduced costs of the process over conventional horizontal EP are potentially significant.

Faraday is designing and building a simple cavity polishing apparatus for Oak Ridge National Laboratory that enables cavity processing in the vertical orientation, without the need for expensive features such as rotary seals and sliding electrical contacts. Furthermore, as we are using dilute sulphuric acid or near-neutral aqueous electrolytes, the need for hydrofluoric acid resistant materials is eliminated, also lowering the capital cost.

Figure 3 shows a schematic of the simple fixturing used to hold and align the cavity for insertion of the DSA anode rod and subsequent processing. Figure 4 shows an ORNL cavity loaded into the apparatus, and oriented vertically. While preliminary experiments on the ORNL cavity have just begun (Figure 5), in preliminary activities we have correlated the anodic current transient indicative of "cathodic" electropolishing.

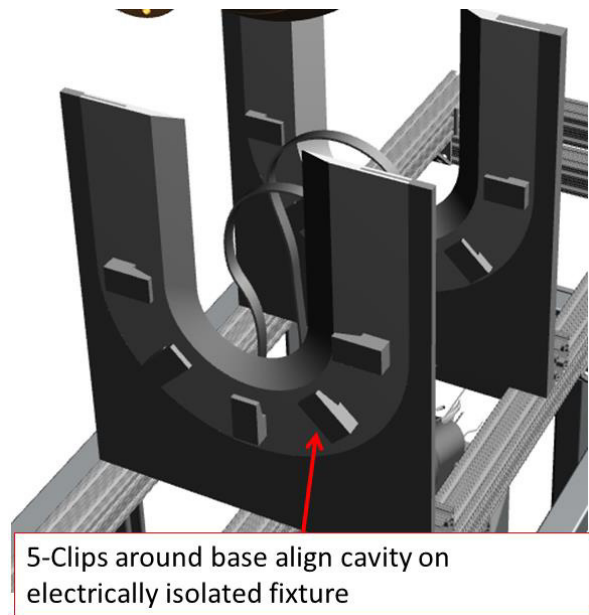5-Clips around base align cavity on electrically isolated fixture

Figure 3: Simple fixturing for holding cavity in place during processing in Faraday's vertical apparatus being built for Oak Ridge National Laboratory.
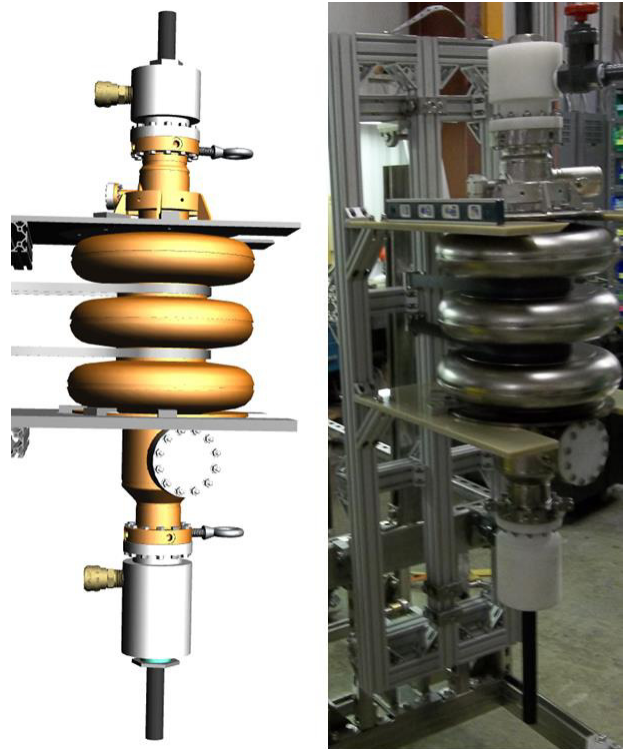

Figure 4: Vertical cavity electropolishing apparatus with cavity in place, being built for Oak Ridge National Laboratory.

Figure 5: Initial vertical electropolishing trials with Oak Ridge National Laboratory three-cell cavity.

SUMMARY

We report on recent development activities directed towards an "eco-friendly" electropolishing process for niobium SRF cavities. Bipolar EP for bulk and final electropolishing steps uses a dilute aqueous sulphuric acid electrolyte without the addition of hydrofluoric acid, and has been demonstrated in single cell cavities. Coupon studies have also demonstrated the ability to electropolish niobium in completely acid-free electrolytes, at near-neutral pH. Ra values lower than 0.2 µm have been achieved in an electrolyte of 200 g/L potassium chloride with 3 g/l monobasic potassium phosphate, at removal rates exceeding 40 µm/hr.

The Bipolar EP process operates in a vertical cavity orientation, filled with electrolyte and without rotation. Consequently, Bipolar EP offers numerous advantages from an industrial processing perspective. Activities are ongoing in simplified apparatus design, build and testing, and results will be reported in future publications.

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