

Final Technical Report for DE-FG02-06ER41434

“Research and Development for Electropolishing of Nb for ILC Accelerator Cavities”

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1. Project Objectives from the Original Proposal

The objectives of this project are to 1.) Expand the scientific and technological understanding of the effect of post-treatment (electropolish, buffered chemical polish, low-temperature baking) on the surface of niobium. 2.) Relate the knowledge to the performance of niobium superconducting radiofrequency accelerator cavities. 3.) Thereby design and demonstrate an electropolish process that can be applied to complete cavities. Studies with complete cavities are planned for a successor to this proposal. See Proposed Work below for how these objectives will be attained.

2. Previously Reported Progress (from Submitted Progress Report)

Our effort in these nine months emphasized 1.) Fundamental EP Studies. The VT and W&M doctoral students supported by this grant have constructed instrumented lab EP units and collected new, fundamental data under conditions related to real cavity processing. JLab workers set up EP units for single cell and for full ILC cavities. The involvement of an electrochemist (Prof. Sean Corcoran at VT) has proven crucial. 2.) Performance Enhancement by Low Temperature Baking. We have completed a study of the effect of such treatment on surface chemistry and correlated that with performance measurement in equivalently-treated single cell cavities. 3.) System for SRF Performance Measurements on Flat Discs. A painful aspect of materials surface studies related to SRF is that we never do performance measurement and characterization on the same sample. JLab workers and a JLab-funded doctoral student built a novel TE₀₁₁ mode 7.5 GHz cavity Surface Impedance Characterization (“SIC”). It is being commissioned now and will accommodate 50 mm diameter discs, as do our characterization facilities. We have presented our results at the Tesla Technology Collaboration meeting (4/23-26/07) and SRF Materials Workshop (FermiLab, 5/23 & 24/07). We are scheduled to present all the above work at the Beijing SRF meeting this fall. What we have learned has been fed back into cavity processing at JLab.

3. Activity Since Progress Report

The ultimate purpose of applying EP to the SRF cavity internal surface is to operate the process in a way that smoothes the surface to attain the desired SRF performance. Accordingly, the central objectives of our efforts were to characterize Nb surface topography and to understand the EP process.

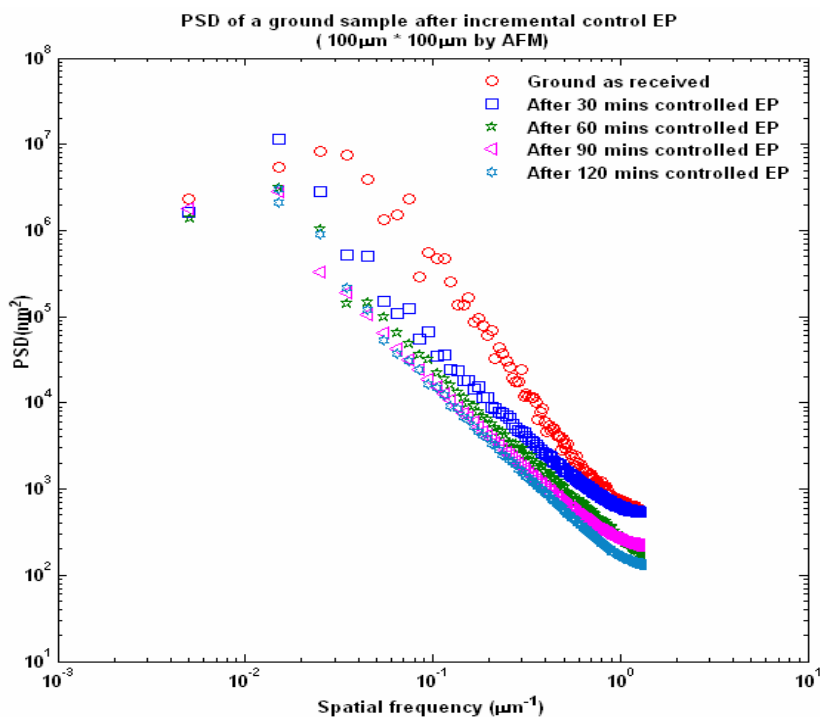
3.1 Topography characterization must be reliable, reproducible and reveal the important features. Scanning probe methods (SPM's) are now widely used – stylus

profilometry (SP) and atomic force microscopy (AFM). The resulting datasets consist of the vertical (normal to the surface) position at which the probe encounters the surface at a series of points along a straight line (trace or scan). The vertical resolution can be better than a nanometer for AFM. The lateral resolution cannot be smaller than the probe tip dimensions, about a micron for SP and a few nm for AFM. Further, lateral resolution cannot be better than the spacing between adjacent points. SPM instruments are configured to collect a chosen number of datapoints per scan, so that closer spacing (= greater lateral resolution) necessarily results in less area being scanned or more scans being acquired. As with all experiments, it must be decided how many datasets obtained with what parameters are needed to adequately represent the sample.

Scanning probe data are typically described by a single roughness parameter, such as the average or rms difference of the actual vertical position of the probe from the average over all the points comprising the scan: Ra or Rz. We reported [1] that measuring four locations on seven samples from two different niobium batches (total 28 values for each) after BCP gave Ra values of 1.66 microns and 1.61 microns, with standard deviations of 0.55 microns and 0.48 microns, respectively, a distinct lack of precision. In comparing EP and BCP for single crystal and standard polycrystalline sheet, we found Ra values of 0.3 and 0.1 microns for EP of polycrystal and single crystal material, with 0.6 microns for BCP of single crystal compared to the 1.6 microns for polycrystalline sheet. While these differences are consistent with the well-accepted notions that EP is smoother and grain boundaries contribute to roughness, they afford little real insight. A further complication for the use of Ra is that the value depends on the size of the area examined, since the probability of encountering less-frequent extreme features increases as more area is examined [2, 3]

The most significant shortcoming of such single or lumped parameter descriptions is that information about the lateral scale is discarded. Accordingly, no insight is obtained into the sharpness of the surface topography, an aspect of great interest here. When similar issues faced the optics and thin film communities, they developed Fourier-transform methods to extract lateral as well vertical displacement information [4], providing a direct view of “sharpness” in terms of amplitude at wavelength. Surface roughness characterization by power spectral density (PSD) has been adopted as a standard for silicon wafers [5] and a draft standard for optics [6].

We have completed a first phase of investigating the application of PSD methods to Nb SRF surface topography [2, 3]. Briefly, a series of AFM and SP scans are obtained from several surface locations the specimen according to the protocol developed, and the squares of the Fourier transforms are combined as a plot of PSD versus spatial frequency (inverse of wavelength). The lateral range extends from well above the nominal 100 micron grain size down to well-submicron. The chief barrier to going lower still is the added data collection effort. A break in the slope is evident at about the grain size, indicating that grain-to-grain differences in surface topography have a different character from within-grain differences. Further, it is evident that PSD's from different SP and AFM scans can be readily combined to give a single picture.



The figure shows PSD's obtained from a surface of a flat sheet sample, as-ground and after EP treatments of successively greater duration, each in fresh solution. The chief initial effect is to reduce roughness at a lateral scale (10 to 100 microns) approaching the grain size, with little impact at the near-micron scale. The effect of doubling the treatment duration is most evident at the near-micron scale. Extending the treatment duration further produces only a small effect.

While more data are certainly needed, it would appear that the benefit of EP under these conditions is achieved by 60 minutes. The main point, however, is that SP and AFM data analyzed and combined as the PSD provides a means to directly view the effect of surface processing in terms of the features that are understood to matter for performance. Unfortunately, the complete PSD for each treatment duration required a full day's effort by an experienced operator.

3.2 Electropolishing (EP) attracted interest for Nb SRF cavity interiors as early as buffered chemical polishing (BCP), but EP's greater process complexity deferred its introduction so long as the simpler BCP process yielded adequate performance. Now the broad consensus in the SRF community is that BCP will not be able to reliably, routinely and affordably produce cavities that meet the increasingly stringent demands of future accelerators, lending high priority to EP process development. Both EP and BCP rely on hydrofluoric acid (HF) to remove the oxide film so that etching can proceed. Eliminating HF is attractive in terms of environmental friendliness, safety and cost.

The EP process now applied to cavities was inherited from Siemens Company in the 1970's [7] and was further developed by KEK in collaboration with Namura Plating [8]. Typically, a mixture of hydrofluoric (49%) and sulfuric acid (95 ~98 %) at a volume ratio of 1 : 9 is used with a temperature range of 30 °C ~ 40 °C, a current density of 30 ~ 100 mA/cm², and a total cell voltage of 10~20 volts. The surface area ratio of the Nb

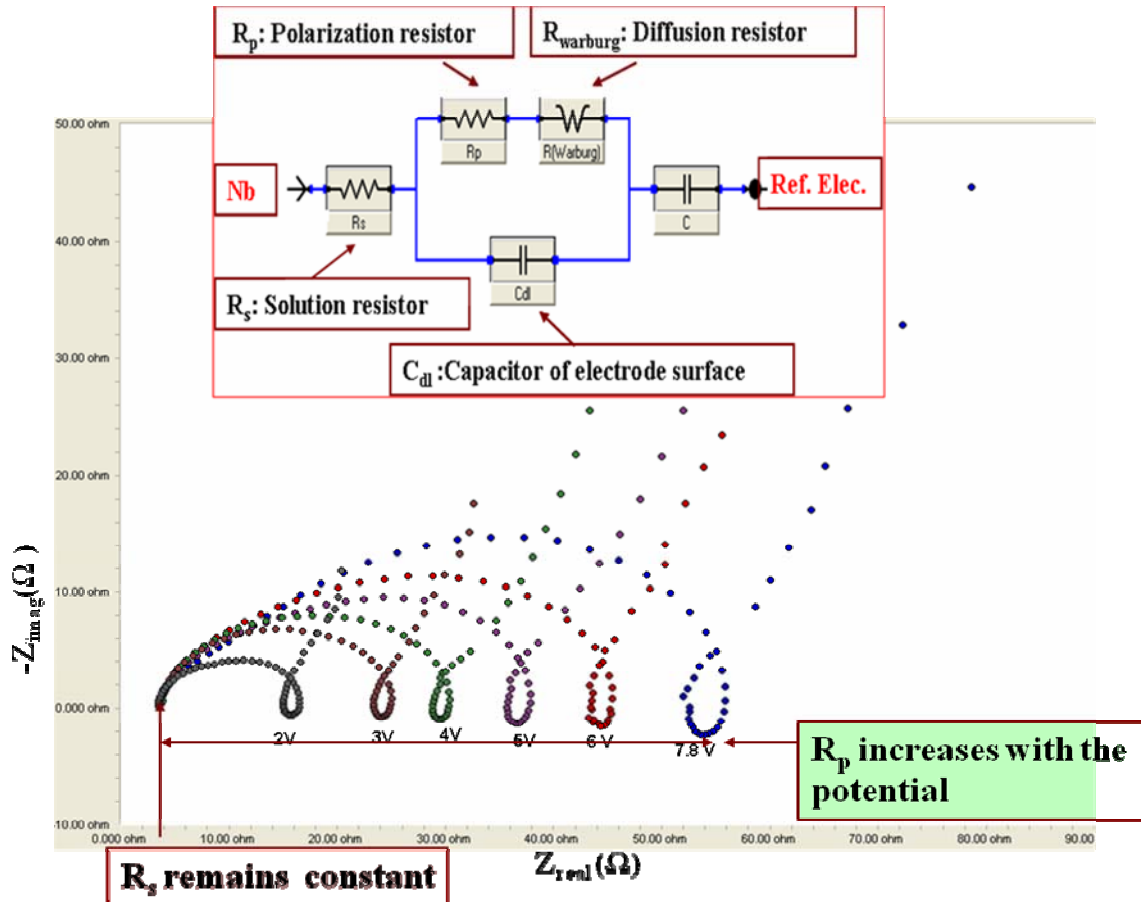
cavity (anode) to the high purity Al tube cathode is 10: 1 during practical cavity EP processing. The most common set-up places the cavity axis horizontal with the cathode tube on the axis. Fluid enters through cathode via a port at each cell and exits through the beam tubes at each end. The cavity is about 60% filled to allow the exit of hydrogen produced at the cathode and rotates at about 1 RPM. Researchers at Cornell have recently described an alternative EP process, wherein the cavity is fixed with its axis vertical [9, 10]. In addition to being mechanically simpler, vertical EP permits steady-state, rather than interrupted, polishing to be established at the cavity surface and can more readily accommodate external cooling for better process temperature control.

Previous cavity EP studies have shown that the best polishing condition occurs in the current-limited plateau of the polarization curves. Parameters such as electrolyte temperature, acid concentration, viscosity and stirring have strong effects on the EP process [11]. Some studies conducted on either small samples or half cells tried to evaluate the influence of each parameter [12, 13]. The electrochemical measurements were limited to total cell voltage and current, which did not reveal sufficient information to yield a clear picture of the exact role of each parameter involved during the EP process.

We recently completed a first phase electropolishing study [14, 15], in which we introduced the use of multi-electrode cell studies and electrochemical impedance spectroscopy (EIS). Briefly, studies using three (or more) electrodes place an added (reference) electrode adjacent to the anode or (and) cathode, so that the potential drop at each and across the solution can be measured separately, in contrast with simply measuring their sum as the cell voltage and current as has been done previously. Important findings include: 1.) the cathode is able to carry the current, even though its area ratio is small, and its voltage drop is purely resistive 2.) the voltage drop across the solution is a few volts and is purely resistive 3.) the anode shows a plateau (current constant with increasing voltage) from 2-3 volts out to near 15 volts. The plateau current increases linearly with HF content and exponentially with temperature.

EIS takes advantage of the fact that each electrode with its population(s) of associated ions is a capacitor that can be probed in the manner of a resistor-capacitor network [16]. Briefly, primary conditions (voltage, DC current, etc.) are set and the cell is allowed to reach steady-state. A small AC signal is imposed on the main DC and its frequency is varied from sub-Hz to a few hundred kHz while the impedance is measured. The real and imaginary parts of the impedance are cross-plotted (Nyquist plot), here for a series of anode voltages. In the schematic circuit illustration above, C_{dl} represents the capacitance associated with the ions comprising the double layer at the anode, R_s is the resistance of the (bulk) solution (which remains constant) and R_p is the resistance at the anode (which increases with voltage to maintain the plateau). The six individual EIS scans combined here were collected at a series of anode voltages along the current plateau at 5.5 °C in 1:9 mixed acid. The discussion leading to the conclusions is rather too lengthy to present here, but appears in the references [14]. The mechanism consistent with all the data is that a compact salt film (probably Nb₂O₅) covers the surface and the

polishing rate is controlled by diffusion of F⁻ (or a related species) through a near-surface depleted zone.



Surface features protruding different distances into, even through, the diffusion layer will see different concentrations of fluoride ion. Since the material removal rate increases with concentration, the largest features will be attacked most: leveling. Further, provided that indeed diffusion through the fluoride-depleted layer is the slow step rather than surface reaction, the removal rate will be the same at all surface locations having the same concentration: polishing. A focusing issue is therefore understanding and managing the diffusion layer relative to the surface topography. While there is certainly much more to be learned, the results so far provide a framework within which to structure future research and process development efforts.

4. Future work.

On going work is needed to further lay the fundamental research basis for SRF cavity surface design. To accomplish this we will seek support to 1.) extend our previous advances in fundamental understanding and measurement of surface topography and electropolishing to include all the major aspects relevant to SRF cavities for the present

and next-generation processes and 2.) apply the knowledge gained to cavity processing and correlated with measured SRF performance.

5. References

1. H.Tian, Charles E. Reece, Michael J. Kelley, Shancai Wan, Lukasz Plucinski, Kevin E. Smith, Matthew M. Nowell; Appl.Surf.Sci. 253 (2006) 1236-1242 “Surface studies of niobium chemically polished under conditions for superconducting radio frequency (SRF) cavity production”
2. H.Tian, G.Ribeill, M.J.Kelley, C.E.Reece; Proc. Beijing SRF Conf. “Surface roughness characterization of niobium subjected to incremental BCP and EP processing steps”
3. Hui Tian PhD Dissertation, Dept. of Applied Science, College of William & Mary, August 2008.
4. J.M.Elson, J.Bennett; Appl.Optics 34 (1995) 201-208 “Calculation of the power spectral density from surface profile data.” A series of papers from these authors spanning nearly twenty years is referenced.
5. anon; SEMI MF1811-0704; SEMI (available for purchase) “Guide for estimating the power spectral density function and related finish parameters from surface profile data”
6. anon; ISO 10110-8: 1997; International Organization for Standardization (available for purchase) “Optics and optical instruments-Preparation of drawings for optical elements and systems – Part 8: Surface texture”.
7. H. Diepers, O. Schmidt, H. Martens and F.S.Sun , Phys. Lett., 37(A), 139 (1971)
8. K. Satio, Y. Kojima, T. Furuya, S. Mitsunobu, S. Noguchi, K. Hosoyama, T. Nakazato, T. Tajima, K. Asano, K. Inoue, Y. Iino, H. Nomura and K. Takeuchi, 2, Proc. of 4th SRF workshop, KEK, Tsukuba, Japan (1989).
9. R.Geng, A.C.Crawford, H.Padamsee, A.Seaman; Proc. 9th SRF Workshop, Ithaca 2005, ThP04 “Vertical electropolishing of niobium cavities”
10. H.Padamsee, A.C.Crawford, A.Favale, M.Cole, J.Rathke, M.Pekeler, W.Ashmanskas; Proc. PAC 07, Albuquerque 2007 “Results on 9-cell ILC and 9-cell re-entrant cavities”
11. V. Palmieri, Proc. of 11th SRF workshop, Travemünde/Lübeck, Germany (2003).
12. F. Eozénou, A. Aspart, C. Antoine and B. Maliki. CARE Report 06-10-SRF. EU contract number RII3-CT-2003-506395 (2006)

13. C. Boffo, P. Bauer, T. Reid and R. Geng, Proc. of 12th SRF workshop, Ithaca, NY, USA (2005).
14. Hui Tian, Sean G. Corcoran, Charles E. Reece, Michael J. Kelley; J.Electrochem.Soc. 155 (2008) D563-D568. "The mechanism of electropolishing of niobium in hydrofluoric-sulfuric acid electrolyte"
15. H.Tian, S.G.Corcoran, M.J.Kelley, C.E.Reece; Proc. 13th SRF Workshop, Beijing, China (2007) "Novel characterization of the electropolishing of niobium with sulfuric and hydrofluoric acid mixtures"
16. Mark E. Orazem, Bernard Tribollet; "Electrochemical impedance spectroscopy" Electrochemical Society Monograph Series, Wiley-Interscience (2008).

6. Publications From This Work

1. Hui Tian, Sean G. Corcoran, Charles E. Reece, Michael J. Kelley; J.Electrochem.Soc. 155 (2008) D563-D568. "The mechanism of electropolishing of niobium in hydrofluoric-sulfuric acid electrolyte"
2. H.Tian, S.G.Corcoran, M.J.Kelley, C.E.Reece; Proc. 13th SRF Workshop, Beijing, China (2007) "Novel characterization of the electropolishing of niobium with sulfuric and hydrofluoric acid mixtures" DOE/OR/23177-0312. OSTI ID: 923387
3. H.Tian, G.Ribeill, M.J.Kelley, C.E.Reece; Proc. 13th SRF Workshop, Beijing, China (2007) "Surface roughness characterization of niobium subjected to incremental BCP and EP processing steps" DOE/OR/23177-0314. OSTI ID: 923389
4. Hui Tian, Binping Xiao, Michael Kelley, Charles Reece, A. DeMasi, L. Piper, Kevin E. Smith Jr.; "Recent XPS Studies of the Effect of Processing on Nb SRF Surfaces". DOE/OR/23177-0313. OSTI ID: 923388

7. Dissertations

Hui Tian. "Surface Study of Niobium for Superconducting Radio Frequency (SRF) Accelerators" PhD dissertation, Department of Applied Science, College of William & Mary. (degree awarded August 2008)