Surface Polishing of Niobium for Superconducting Radio Frequency (SRF) Cavity
Applications

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ABSTRACT

Niobium cavities are important components in modern particle accelerators based on superconducting radio frequency (SRF) technology. The interior of SRF cavities are cleaned and polished in order to produce high accelerating field and low power dissipation on the cavity wall. Current polishing methods, buffered chemical polishing (BCP) and electro-polishing (EP), have their advantages and limitations. We seek to improve current methods and explore laser polishing (LP) as a greener alternative of chemical methods.

The topography and removal rate of BCP at different conditions (duration, temperature, sample orientation, flow rate) was studied with optical microscopy, scanning electron microscopy (SEM), and electron backscatter diffraction (EBSD). Differential etching on different crystal orientations is the main contributor to fine grain niobium BCP topography, with gas evolution playing a secondary role. The surface of single crystal and bi-crystal niobium is smooth even after heavy BCP. The topography of fine grain niobium depends on total removal. The removal rate increases with temperature and surface acid flow rate within the range of 0~20 °C, with chemical reaction being the possible dominant rate control mechanism. Surface flow helps to regulate temperature and avoid gas accumulation on the surface.

The effect of surface flow rate on niobium EP was studied with optical microscopy, atomic force microscopy (AFM), and power spectral density (PSD) analysis. Within the range of 0~3.7 cm/s, no significant difference was found on the removal rate and the macro roughness. Possible improvement on the micro roughness with increased surface flow rate was observed.

The effect of fluence and pulse accumulation on niobium topography during LP was studied with optical microscopy, SEM, AFM, and PSD analysis. Polishing on micro scale was achieved within fluence range of 0.57~0.90 J/cm², with pulse accumulation adjusted accordingly. Larger area treatment was proved possible by overlapping laser tracks at proper ratio. Comparison of topography and PSD indicates that LP smooths the surface in a way similar to EP. The optimized LP parameters were applied to different types of niobium surfaces representing different stages in cavity fabrication. LP reduces the sharpness on rough surfaces effectively, while doing no harm to smooth surfaces. Secondary ion mass spectrometer (SIMS) analysis showed that LP reduces the oxide layer slightly and no contamination occurred from LP. EBSD showed no significant change on crystal structure after LP.

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Surface Polishing of Niobium for Superconducting Radio Frequency (SRF) Cavity Applications

CHAPTER 1

Introduction

1.1. Motivation

1.1.1. Accelerators and superconducting radio frequency (SRF) technology

Particle accelerators are a vital scientific research tool, serving high energy and nuclear physics since their earliest days. Their continuing progress depends on continuing progress in accelerator science and technology; the Large Hadron Collider (LHC) and the envisioned International Linear Collider (ILC) are the most visible examples. Elsewhere, advanced particle accelerators are gaining increased attention as drivers for next-generation light sources; the Linac Coherent Light Source (LCLS) I & II are examples.

The most significant barrier to progress in all cases continues to be the initial and operating costs. Superconducting radiofrequency (SRF) technology, though itself costly, has reduced the “unit cost of beam” to make the present generation of frontier machines viable. The future depends on further cost reductions. A major target is the cryoplant investment and electric power to operate at the 1.8 K – 2 K temperature required by today’s solid niobium technology. While alternative materials may emerge as an option eventually, proposed and existing SRF machines will depend on solid niobium. Energy consumption in SRF accelerator cavities is described by the cavity quality factor, Q_0 , the

ratio of resonant microwave energy stored in the cavity and available to accelerate particles, to the energy deposited in the cavity walls, which must be (expensively) removed by the cryosystem. The most common representation of accelerator cavity performance is a plot of quality factor versus acceleration gradient (Figure 1.3). A detailed discussion appears later. For the present, suffice it to note that improved performance means higher Q_0 , especially at high gradients.

Particle accelerator projects and facilities are widely spread around the world and have several categories according to the usage of the beam. Table 1.1 summarizes some examples of past, present and future projects.

Table 1.1. Examples of particle accelerator projects

Circular and linear collider	LEP and LHC [1] (European Center for Nuclear Research-CERN), HERA [2] (Deutsches Elektronen-Synchrotron-DESY), Tevatron [3] (Fermi National Accelerator Laboratory-FNAL), Electron-positron Storage Ring (CESR) [4] (Cornell), Relativistic Heavy Ion Collider (RHIC) [5] (Brookhaven National Laboratory-BNL), ILC [6], Compact Linear Collider (CLIC) [7], TRISTAN [8] and B-factory [9] (KEK, Japan), BEPCII [10] in China, etc.
Synchrotron light source	SOLEIL [11] (France), Shanghai Synchrotron Radiation Facility (SSRF) [12] (China), National Synchrotron Light Source (NSLS) [13] (BNL), Diamond Light Source [14] (UK), Advanced Light Source (ALS) [15] (Lawrence Berkeley National Lab-LBNL), Advanced Photon Source (APS) [16] (Argonne National Lab-ANL), European

	Synchrotron Radiation Facility (ESRF) [17] (Grenoble, France), etc.
Free Electron Laser (FEL)	European XFEL [18] (DESY), FLASH [19] (DESY), Linac Coherent Light Source (LCLS) [20] (SLAC), FEL (Jefferson Lab) [21], etc.
Fixed target beam	Continuous Electron Beam Accelerator Facility (CEBAF) [22] (Jefferson Lab), Facility for Rare Isotope Beams (FRIB) [23] (Michigan State University), Spallation Neutron Source (SNS) [24] (Oak Ridge National Laboratory-ORNL), SPIRAL2 [25] (GANIL, France), ISAC-II [26] (TRIUMF, Canada), European Spallation Source (ESS) [27] (Sweden), etc.

These accelerators, many of which use SRF technique, bring advances in fundamental physics, applied research and technology. Collaboration around the world enhances communication within the scientific community and economic development between countries.

1.1.2. SRF cavity

Radio frequency (RF) cavities are used to provide energy to particles in particle accelerators. Such RF cavities can be categorized into normal conducting and superconducting (SRF) cavity varieties. Normal conducting cavity is made of copper and operates at room temperature with water cooling. They can reach very high accelerating gradient (E_{acc}) of hundreds of MV/m but only in pulsed mode, due to heating of the cavity. Superconducting cavities are mostly made of niobium and operate at temperatures of 2 - 4.2 K with liquid helium cryostat cooling. They can reach an E_{acc} of 50 MV/m in

continuous wave (CW) mode. Niobium SRF cavities can achieve quality factors (Q_0) 10^5 to 10^6 times that of copper normal conducting cavities [28]. The advantages of SRF compared with normal conducting RF are reduced RF capital and reduced RF-associated operating costs due to the low cavity wall losses [29].

SRF cavities are hollow metal structure with different shapes and often a wall thickness of about 3 mm. The scope of the thesis focuses on bulk niobium, which is used in most projects nowadays. Research efforts of depositing niobium thin film on copper cavity and using other superconducting materials to substitute niobium are on-going at several institutes. The electro-magnetic field distribution inside SRF cavities varies depending on their shapes and operating modes. Figure 1.1 is a picture of an ILC nine-cell cavity. And Figure 1.2 shows schematically the field distribution within a single cell elliptical cavity. For the commonly used TM_{010} mode, the peak electric field is at the iris, and the peak magnetic field is at the equator.

Figure 1.1. Nine-cell 1.3 GHz superconducting niobium cavity for ILC design baseline

[30]

Figure 1.2. Electric and magnetic field distribution within a single cell [28]

One important figure of merit for RF cavities is the quality factor Q_0 , also called the intrinsic Q of the cavity. It describes the ability of a cavity to store energy. It is the ratio of stored power in the cavity to the dissipated power on the cavity inner wall. Given cavity geometry, Q_0 depends on the microwave surface resistance of the metal, usually in the order of $10^9 - 10^{10}$. Another important characteristic of an RF cavity is the average accelerating field, E_{acc} , which describes the ability of a cavity accelerating a particle, from a few MV/m up to 50 MV/m. The Q_0 - E_{acc} curve is usually the benchmark used to evaluate the performance of a cavity in the SRF community.

Theoretically the accelerating gradient of SRF cavities is limited by the superheating magnetic field, when the transition from superconducting to normal conducting happens. In reality, SRF cavity performance is usually lower than this theoretical value and often limited by a few other mechanisms, such as field emission and multipacting, before

reaching theoretical limit. The limiting mechanisms are often related to surface impurities and/or defects. For normally functioning cavities, Q-slope could happen at low and medium field due to variation of the surface resistance, as shown in Figure 1.3. Poor functioned cavities could show significant Q drop at low gradient, such as Q-disease and Q-switch [28]. The end of the Q_0 - E_{acc} curve is usually caused by a quench, in which a thermal breakdown (a significant loss of superconductivity) is caused by different mechanisms, such as local hotspot or defects, or global heating effect.

Figure 1.3. Q-slope and Q-drop in Q_0 - E_{acc} plot [31]

Field emission is an important factor limiting cavity performance at gradients below 25 MV/m [28]. High electric field regions on the cavity surface are most susceptible to field emission. The emitted electrons could consume significant amount of RF power. Accelerated by the electromagnetic field, they could hit the cavity wall, produce heat and generate x-rays. They could also knock out more electrons by impacting the cavity wall and cause multipacting if a large number of electrons were build up under certain resonant frequency. Field emitters could be particles or sharp features introduced during the surface treatment or cavity assembly. Some of them can be removed by RF processing or "conditioning", while others cannot.

Q slope happens through almost the entire Q_0 - E_{acc} curve, with different behaviors at different stages, so called low field Q-slope, medium field Q-slope, and high field Q-drop. Several models have been proposed to explain this phenomenon and fit the experimental data [31] [32] [33]. Q slopes at medium and high field are RF losses caused by local defects ("hot-spots") on the cavity [32] [34] [35], and occur in the high magnetic field region of the cavity. The source of the hot-spots could be magnetic vortices, lattice dislocations and/or vacancies near the surface, hydrogen [34]. A magnetic field enhancement model suggested surface sharp features could be responsible for degradation of high-field Q [33].

Quench, also known as the thermal breakdown, starts from Joule heating at local defects or global losses. And when the heat transport through the cavity wall is not fast enough to maintain the superconducting state of the material, a normal conducting region appears and grows, resulting in more power dissipation, and eventually cavity breakdown. Methods to overcome early thermal breakdown include: repairing defects by local or entire cavity surface treatment; raising thermal conductivity of niobium by improving purity (or increasing RRR) of the material, such as heat treatment; coating thin films of niobium on copper, etc.

1.1.3. Surface resistance

In an SRF cavity filled with RF power, electromagnetic field enters the superconducting niobium surface with ~ 40 nm penetration depth (λ) (the intensity of the field inside the niobium falls off exponentially from the surface at $\sim e^{-x/\lambda}$) and interacts with charge carriers, causing RF power to dissipate onto the cavity wall, described by an effective surface resistance (R_s). The quality factor Q_0 can be calculated from R_s :

$$Q_0 = \frac{G}{R_s}$$

where G is a geometry constant which depends on the cavity shape and mode but not its size.

This effective resistance is an average value representing the property of the entire inner surface, while in reality the surface resistance is not uniform. A simplified form of the surface resistance for $T_c/T > 2$ and frequencies much smaller than 10^{12} Hz is [36]:

$$R_s = A(1/T)f^2 e^{-\Delta(T)/kT} + R_0$$

where A is a constant depending on material parameters.

The Mattis-Bardeen theory [37], based on BCS theory [38] and anomalous skin effect theory [39], has been used to explain RF surface resistance in the low field limit. The BCS-Mattis-Bardeen surface resistance, R_{BCS} , depends on the temperature, the RF frequency, and the energy gap 2Δ of the surface material. It decreases exponentially with temperature and increases as the square of the RF frequency below 10 GHz [29]. When a 1.5 GHz cavity is cooled to below 2 K, the BCS resistance becomes less than 20 n Ω [29]. Given temperature and frequency, the magnitude of surface resistance also depends on material parameters, such as the London penetration depth λ_L (64 nm for pure Nb), Fermi velocity, and the electron mean free path (l), which characterizes material purity. However, at $T < 0.2T_c$ the surface resistance does not fall exponentially with temperature towards zero as predicted by BCS. Rather, there are always some residual losses which are temperature independent. Taking the residual resistance into account, now a common understanding is that surface resistance (R_s) is composed of BCS resistance (R_{BCS}) and residual resistance (R_0). Residual resistance may come from surface impurities introduced by chemical etching and machining. Additionally, surface defects,

trapped magnetic flux, hydrides and oxides are also responsible for increased surface residual resistance. The lowest R_s reached by a well prepared niobium SRF cavity is 1~2 n Ω at 1.3 GHz and 1.6 K [29].

The performance of SRF cavities is closely related to surface resistance. Lower surface resistance means higher quality factor, which will reduce the cost of operating SRF cavities. Surface resistance strongly depends on the surface layer of the cavity inner wall, which means the surface preparation technique is critical to cavity performance.

1.1.4. Effect of topography on SRF performance

Making SRF cavities from bulk niobium started in the 1960's [40]. Buffered chemical polishing (BCP) was soon applied to clean the interior of niobium cavities [41]. Electropolishing (EP) was developed later [42] to achieve smoother surfaces. People realized that sharp features were likely to be associated with the known performance deficit of SRF cavities, such as Q-drop at higher gradients, due to magnetic field enhancements [43] [33]. A step with a 20° slope angle and a 5 μ m radius of curvature at the transition corner, for example, gives a local field enhancement of 1.6. Field enhancement values for grain boundaries on typical BCP surfaces can be as large as 2.5 [33]. When a local magnetic field is sufficient to exceed the critical field of superconducting niobium, normal-conducting volumes are formed locally. Even if this may be too small to trigger a general quench (in contrast with bigger defects like pits), the cumulative effect will reduce Q_0 significantly with increasing gradient until a quench occurs. Most recently, a numerical model has been developed to connect inner surface topography to SRF cavity performance [44], so that the cavity performance can be calculated from its interior topography, as shown in Figure 1.4. Model calculations

indicate, for example, that the topography resulting from BCP may be expected to adversely impact performance for gradients above ~14-18 MV/m.

Figure 1.4. Model-predicted Q_0 using representative BCP surface topography (diamond), experimental data for CEBAF prototype cavity LL002 with BCP (dot) and EP (square) surfaces [44]

Put it simply, smoother is better. "Smoother" means eliminating both large defects that cause early quenches and small features that contribute to Q-drop. And that is why in recent years the aim has been applying surface science to SRF cavity fabrication and paying attention to understand and control the topography.

1.1.5. Cavity fabrication and surface preparation

As mentioned previously, the inner surface of SRF cavities plays an important role in their performance. The inner surface preparation becomes critical and great care is needed to achieve high performance. The current practice of cavity production is based on state-of-the-art knowledge gained from accumulated experience. Research aiming at understanding and improving current practice is still going on. And the practice is updating accordingly with new insights, to achieve better performance and lower cost. The exploration of new insights mostly falls in the field of material science.

Niobium sheets are produced from ingots and shaped into SRF cavity walls. Mechanical steps in fabricating a cavity from sheet material include deep drawing, cutting, lapping, welding, and tuning. Between these steps, optical inspection is used to identify defects; chemical etching and mechanical grinding are used to remove defects. Once major mechanical steps are finished, a bulk removal about 100 μm is done by chemical polishing (or electrochemical polishing, depending on project), to remove damage layers caused by machining and achieving a smooth surface. High pressure rinsing (HPR) is used to remove residuals from chemical polishing. Heat treatment is often used after wet chemistry or towards the end to remove hydrogen.

Buffered chemical polishing (BCP) is the traditional way for bulk removal of the material. The most used BCP acid consists of 49% hydrofluoric acid (HF), 69.5% nitric acid (HNO_3), and 85% phosphoric acid (H_3PO_4) in a volume ratio of 1:1:2 or 1:1:1 depending the etching rate needed. It is the fastest and most convenient method among all other choices. The etching process is not limited by cavity shape. But the nature of chemical etching results in a surface finish with sharp edges. The surface RMS roughness

is about 5~10 μm for fine grain niobium [36]. BCP is often used in bulk removal of niobium.

Electropolishing (EP) removes the material through electricity and chemicals. The widely used EP acid is a mixture of 49% hydrofluoric acid (HF) and 96% sulfuric acid (H_2SO_4) at a volume ratio of 1:9. The niobium cavity to be polished is the anode and high purity aluminum is used as the cathode. With both electrodes immersed in the acid, a voltage from 8 to 16 V is applied on them, and the current density is kept around 10~50 mA/cm^2 [36]. The cavity can be oriented horizontally or vertically during EP. For horizontal setup, the cavity is 60% filled with the acid and rotates along its longitudinal axis at a speed of 1~2 rpm. The acid flows into the cavity through holes on the aluminum tube inserted through the cavity center, and flows out of the cavity through the end groups on both sides. For vertical setup, the niobium cavity does not need to rotate. The acid flows in from the lower end, fills up the cavity and flows out from the upper end. Stirring arms can be attached to the aluminum cathode for agitation. Due to its complex setup, EP is mainly used on elliptical cavities and only in certain case on cavities with complicate shapes [45]. Although much slower and complex, EP could achieve the smoothest surface on micro scale and enhance cavity gradient. Therefore it is more and more used for last step polishing. EP can produce a surface root-mean-square (RMS) roughness below 0.5 μm [36].

Centrifugal barrel polishing (CBP), also called tumbling, is a type of mechanical polishing. It was applied to niobium cavities to some extent mostly at KEK and DESY years ago [36], and many labs around the world are doing research on CBP recently [46]. It removes material by using abrasive media rubbing against cavity inner surface under

the centrifugal force during tumbling of the cavity. Different sized solid media mixed with liquid are filled into the cavity, and the cavity is rotated in a horizontal orientation at ~100 rpm. The surface finish could be mirror like with a RMS roughness of 1~2 μm [36]. It has lower removal rate than the chemical methods, but has avoided using hazardous chemicals and can eliminate defects. However, a light chemistry is usually needed after CBP to achieve good performance. This method has not been used on large scale production yet.

The surface preparation practice of SRF cavity production differs from lab to lab and from project to project. For example, ILC and XFEL use EP for bulk removal, 2 hours 800 °C baking for degassing/annealing, EP for light removal, 48 hours 120 °C baking; JLab 12 GeV uses BCP for bulk removal, 10 hours 600 °C baking for degassing/annealing, EP for light removal, 24 hours 120 °C baking; Cornell ERL used BCP for bulk removal, 4 days 650 °C baking for degassing/annealing, BCP for light removal, 48 hours 120 °C baking [47].

Optical inspection is an important surface quality control method. It helps keep track of surface modification such as electron beam welding, cavity repairing, and surface treatments. Localized examination is also performed after cold RF test on area predicted by temperature mapping and second sound. Most industrially available optical systems do not work well on SRF cavities due to limited space, complex shape, and big surface area (~1 m²) of the cavities. Laboratories have developed specialized cavity inspection systems of their own. Figure 1.5 shows the optical inspection apparatus used at Jefferson Lab [48]. Commission of a new vertically oriented system for inspecting and characterizing the interior surface topography is underway at Jefferson Lab [49] (Figure

1.6). This will provide quantitative topographic information inside a cavity without destroying the cavity.

Figure 1.5. Optical inspection apparatus for SRF cavities at Jefferson Lab [48]

Figure 1.6. The CavitY CaLibrated Optical Profilometry System – CYCLOPS at Jefferson Lab [49]

1.1.6. Study on surface polishing methods

BCP on niobium SRF cavity started in 1970 [41]. Since then, surface etching using BCP has been commonly used [50], and some knowledge of this polishing method has been gained by surface characterization [43]. One advantage of BCP over EP is, it is not

limited by cavity shape, whether elliptical [51] or other shapes [52] [53]. It is claimed that BCP cavity performance at high field is limited by the sharp features introduced by the etching process, compared with EP which does not introduce any sharpness [54] [55] [56] [57]. Since the main advantage of EP over BCP is the smooth grain boundary, BCP supporters proposed using large grain material for cavity fabrication to reduce the amount of grain boundaries [58] [59] [60] [55].

EP of niobium was originally developed at Siemens back in 1971 [42]. It was brought to attention to the SRF community by Kenji Saito [61]. EP is the preferred polishing method for high gradient projects [62]. Mechanism study on the commonly used recipe [63] and exploration of HF free EP recipe [64] [65] is among the major R&D topics for EP. There are other issues during EP such as sulfur precipitation from the electrolyte [66] [67] [68] [69] [70] [71].

While chemical methods such as BCP and EP are widely in use and effective, the search for greener alternatives has never stopped. CBP was introduced around 2001 [72] and has been under fast development in many labs.

Laser polishing (LP) of niobium is a candidate proposed recently, which is completely different from traditional chemical and mechanical polishing methods. It has the advantage of no wet chemistry and fast processing. By controlling the power density delivered onto the metal surface and the delivery rate, it is possible to achieve partial melting of the surface. Partial melting smoothens any sharp features on the surface while keeping the basic shape of the background.

Other surface processing methods not within the scope of this thesis are plasma etching and plasma cleaning. Plasma etching removes material by applying RF power to

ionize etching gas mixture (oxygen and chlorine at certain ratio) inside the cavity. Plasma cleaning is a milder way of getting rid of contamination particles on cavity inner surface. It is similar to helium processing (or RF processing), which is a method often used during cavity testing. Its advantage is that the cavity does not need to be disassembled during cleaning.

1.1.7. Surface characterization

Optical and electron microscopies are the most widely used for qualitative study of surface topography. Because they are common instruments nowadays and the results are intuitive to understand, they are almost the first methods people refer to. Besides microscopies, we used some other surface probing techniques.

Surface topography is measured by stylus profilometry and atomic force microscopy (AFM) in our study. In both cases, a probe moves along a line on the surface and its vertical position is recorded. One way to evaluate the surface topography in our studies is by roughness. The root mean square (RMS) roughness $R_q = \sqrt{\frac{1}{n} \sum_{i=1}^n y_i^2}$ is the simplest expression of surface roughness. It describes the height deviation from the average height over the measured range. A BCP treated niobium has a typical RMS roughness larger than $2\mu\text{m}$ [36]. However, the RMS roughness can be strongly impacted by the lateral distance scanned; usually R_q increases with the scanning length. In fact, this reflects the limitation of RMS roughness, where the horizontal width of hills/valleys is not considered. The concept of correlation length is introduced to address this problem. The correlation length is the smallest distance above which the topography values are not strongly impacted by distance any more. For fine grain niobium used in SRF cavities, the

correlation length is about 20-50 μm , comparable to grain size. Previous studies on surface roughness were mostly expressed with RMS roughness. Our group [73] [74] [75] developed the power spectral density (PSD) method to obtain more detailed topography information.

Power spectral density (PSD) provides information of contributions at different spatial frequencies. It is obtained by performing a Fourier transform of the scanning probe topography data. Sharp features have more contribution at short wavelengths (high spatial frequencies) compared with gentle undulations of the same vertical amplitude. PSD amplitude is in units of length cubed. The horizontal axis is in inverse-length units. Since topographic images of surfaces are recorded in the form of digitized data of surface height, which is finite and sampled rather than infinite and continuous, discrete Fourier transform is used in our study. Due to reality, some processing of the data is needed before getting the PSD analysis we need, such as bandwidth determination (instrument limitation and scanning parameters), antialiasing (remove instrument noise), de-trending (remove the background to flatten the mean surface), and windowing (eliminate statistical instability from discontinuity at the two end points) [74]. PSD data is further analyzed by describing them with idealized models, such as fractal structure and superstructure models. Each model represents certain typical topography. One may find the measured PSD curves fit with these models at different frequency range. By analyzing of PSD, one can learn the surface evolution during different processes.

BCP treated fine grain niobium has been found to have certain characteristic features in PSD analysis: power falls with increasing frequency; data at high frequencies show a straight line on the log/log plot indicating a power law function; the frequency

dependence of power at low frequency range departs from linear and approaches a constant value. Interpreting with the models, at low frequencies the data fit to a shifted Gaussian reflecting the grain structure and at higher frequencies the straight line reflects the prominent sharp edges. In contrast, PSD data from typical electro-polished surface do not exhibit straight lines on a log/log plot but display two regions of strong curvature [74].

Electron backscatter diffraction (EBSD) is frequently used to study the impact of mechanical deforming and machining on crystal quality of bulk niobium [76] [77] [78]. It is also largely used in thin film studies [79] [80]. We will refer to this technique in Chapter 5 when we think our polishing process may have changed the crystal quality.

Energy-dispersive X-ray spectroscopy (EDS), X-ray photoelectron spectroscopy (XPS) [81] [76], Auger electron spectroscopy (AES) [81] [82], and secondary ion mass spectrometry (SIMS) [83] are all used in identifying elements on niobium surface after various treatments. We used SIMS to examine if laser process changed the surface chemistry on niobium.

Surface studies have been done both on cavities and coupons. However, the information collected from these two types of studies is barely interchangeable. With coupons, surface topography and chemistry study are easy to do, but RF properties cannot be measured without special equipment. With cavity testing, RF performance after certain surface treatment can be measured directly. However, the large interior surface area and the number of components associated with testing a cavity made it difficult to interpret the pure contribution from surface property confidently. Then when coupons are cut out from a cavity, the properties may be changed. To bridge the gap between cavity

testing and coupon measurement, radio frequency surface impedance characterization (SIC) systems are developed [84] to measure the RF surface resistance of precisely prepared samples.

1.2. Where do we stand?

The level of SRF performance seen today is the fruit of many years' effort by the SRF community to overcome contaminant particles, dissolved hydrogen, surface physical defects, reduce trapped flux, and more [36]. Recent progress is the introduction of electropolishing (EP) to replace buffered chemical polishing (BCP), resulting in smoother surfaces and reduced (or eliminated) high-field Q-drop. A promising more recent finding is that suitable treatment in a nitrogen atmosphere followed by EP can raise mid-field Q to previously unattained levels [85], perhaps through control of residual dissolved hydrogen.

Such findings as the foregoing and the large potential impact of progress makes the application of surface and materials science to SRF cavities attractive to our research group. The work examining the effect of the widely-deployed BCP process on topography and chemistry [76] showed the need to better describe topography [86], especially the sharpness of surface features thought to contribute to Q drop. The significantly smoother topography obtained by EP motivated more research to investigate the EP mechanism in detail [63] [87] to define optimum process parameters. Because of its impact on performance, we continued to explore the measurement of topography and analysis of the data in greater detail [74] [75] [88]. The culmination of this line of work was a successful modeling approach [44] to acquire topographic data and calculate the resulting energy deposition with increasing accelerating gradient to predict E_{acc} vs Q_0 for

the first time (Figure 1.4). It is now possible to address the problem of anticipating the maximum useful gradient for a given topography and the reverse problem, the limits on topography imposed by the surface fields associated with a given cavity design.

It is useful to summarize here the main elements of the present situation of processes versus performance. **BCP** is widely practiced, including by commercial vendors. It can be applied to essentially all cavity shapes. It is quick (few microns per minute) and of modest cost. It has received little research attention since the earliest days; people simply use it. A possible limiting factor is the relatively rough topography that results. Numerical modelling indicates serious Q drop for gradients above the upper teens. Is this topography something fundamental or merely an artifact about how BCP is currently done? Further, there is a large legacy base of BCP-treated cavities installed in SRF accelerators. As these are cycled out for refurbishment, can anything be reasonably done to enhance performance? **EP** can be carried out so as to reliably obtain very smooth topographies that can operate at high gradients, even above 40 MeV/m. On-going research continues to strengthen understanding, pointing the way to improving process performance. However, EP requires a cathode to complete the electrical circuit, the niobium article being polished serving as the anode. This is readily accomplished for symmetrical structures, such as the widely employed elliptical cavity. It is a much greater challenge for advanced structures now gaining attention, such as fork and spoke. Further, typical EP delivers a material removal rate less than a tenth of typical BCP, an even more significant penalty considering that greater complexity of EP facilities. Since the rate of removal is controlled by near-surface mass transport of the reactive species, is it possible to increase removal rate by accelerating mass transport without by the same stroke

impairing topographic leveling? **LP** (laser polishing) is only now being investigated for application to SRF cavities. Can it achieve topography comparable to EP? LP is a rapid thermal process, operating far equilibrium, contrasted with the lengthy, high-temperature annealing typical of present cavity manufacturing. Will there be an effect on SRF properties?

A clear agenda emerges. A BCP process yielding EP-like topography would be the most desirable outcome. The first priority is attaining a detailed fundamental understanding of BCP that leads to that outcome or to the conclusion that BCP inherently cannot deliver topography very different from the present situation. If indeed the latter is the case, the second priority is to seek how to increase the removal rate in EP without compromising performance. If progress on this front cannot be made, the final agenda is to determine the LP parameter range for producing EP-like topography and for treating discs that can be studied in the SIC instrument. If LP is not successful, the message to cavity designers is: 1.) try to keep surface fields below values corresponding 15-18 MeV/m and process with BCP. 2) design symmetric structures that can readily accommodate a cathode and trade the increased process cost of doing EP against the value of increased performance.

1.2.1. Objectives

Our goal is to improve polishing techniques for niobium. That includes:

- Explore potential improvement in existing techniques based on a better understanding of the process;
- Explore potential new techniques.

We would like to:

- Make BCP surface smoother and EP faster by changing polishing parameters;
- Find ways to achieve similar surface finish as EP.

1.2.2. Challenges

Challenges in improving surface polishing techniques include: How to make polishing cheaper, greener, and faster? How to evaluate the smoothness of the surface? How smooth is smooth enough? While developing ways to improve current process, we also need to consider: How can we relate sample study to cavity performance? How to scale sample preparation techniques to cavities? We may not be able to answer all these questions in this work. But our efforts will be part of a continuous team work from past [73] [84] [89] and future generation, which helps collecting pieces of findings and putting together a big picture [90].

1.3. Organization of the dissertation

Chapter 2 presents a systematic study on the mechanism of BCP and the genesis of BCP topography. The reaction mechanism was learned through Arrhenius plot. Factors affecting topography such as temperature, polishing duration, surface flow, surface orientation, sample grain size, crystal orientation, and bubble generation were studied using optical microscope, scanning electron microscope (SEM), atomic force microscope (AFM), and electron backscatter diffraction (EBSD). Then the heat and mass transfer during BCP were also considered.

Chapter 3 studies the effect of surface flow rate on the finishing topography of niobium during EP. Niobium EP with different surface flow rates was conducted and the

resulting topography was characterized by optical microscope, AFM, and power spectral density (PSD). The influence of surface flow was also discussed in mass transport point of view.

Chapter 4 presents the optimization of laser polishing parameters for niobium by finding the best combination of fluence and pulse accumulation. A one-dimensional conduction heat transfer model was used to calculate surface temperature profile and understand polishing mechanism. The topography was evaluated with optical microscope, SEM, AFM, and PSD. Larger area laser polishing was carried out by overlapping multi laser tracks at different ratios.

Chapter 5 presents the application of laser polishing with optimized parameters on surfaces prepared using different methods. The types of surface include BCP, CBP, mechanical polished, and nano-polished niobium surfaces. The effects of laser polishing on topography, surface roughness, surface chemistry, and crystal orientation are described.

Chapter 6 summarizes our accomplishments and proposes future work. We obtained further understanding in BCP and EP, which will help making better SRF cavities. We achieved encouraging result from laser polishing, which gives hope for a game-changing future technique.

CHAPTER 2

Genesis of Topography in Buffered Chemical Polishing (BCP) of Niobium

2.1. Introduction

Mechanical fabrication and welding leave a damaged layer on the niobium cavity interior surface that must be removed before use. Acid etching (details below) has been used since the earliest days. The resulting topography displays micron-scale roughness [76]. Numerical modeling [44] indicates that such topography will significantly absorb RF energy a fields corresponding to gradients above the 15 – 18 MeV/m range, making them unsuitable for SRF use. Nonetheless, the process is convenient and affordable relative to alternatives. Further, the complex interior geometry of new SRF cavity shapes is quite compatible with acid etching. A fundamental investigation in hope of finding a path to improved results is needed.

2.1.1. History of BCP and current practice on cavities

Buffered chemical polishing (BCP) has been used for niobium SRF cavities for more than forty years since the first report of use in 1970 [41]. As BCP is practiced today, the recipe for BCP acid is usually composed of a 1:1:1 or 1:1:2 (volume) mixture of 69.5%

nitric acid, 49% hydrofluoric acid, and 85% phosphoric acid. BCP is usually the first choice for a bulk removal about 100~200 µm of the surface material because of its fast removal and simple setup. For parts cleaning and sample etching, it is as simple as immersing the sample in the acid mixture for certain amount of time, with water/ice bath cooling and agitation if necessary. For large cavity etching, a closed system with acid circulation and cooling is needed. In Jefferson Lab, the acid mixture in the tank is cooled down below 10°C and pumped into a vertically positioned cavity from the bottom. The acid fills up the cavity and flows out from the top. As the chemical reaction generates heat, the acid needs to be cooled throughout the polishing process. The acid temperature should be kept below 15°C to reduce the risk of hydrogen contamination [50] which could cause "Q-disease" of the cavity. To avoid different removal rates of the upper and lower half cells in the vertical setup, the cavity is usually polished in two cycles and flipped over between cycles. After BCP, the cavity is extensively rinsed with de-ionized water flowing through the cavity, and later sprayed with high pressurized ultra-pure water to remove any residuals from the etching.

2.1.2. Current understanding about BCP

The understanding of BCP reaction is that HNO₃ oxidizes niobium metal to niobium pentoxide, which is then dissolved by the HF. The actual solution species are doubtless more complex. The function of H₃PO₄ is to limit the rate of the reaction as a buffer. The reaction steps could be complicated, although one possible description of the process can be written as [50]:

The brownish smoke coming out of the solution is NO₂, the reduction product from HNO₃. The heat of reaction was experimentally determined to be about -607 kJ/mol [91], corresponding to 5.6 J/cm² per μm removed. Copious nitric oxide (NO) is also generated – nominally about 0.3 mL per μm removed for Malloch's reaction scheme [91]. Others envision NO₂ production instead, leading to ~ 1 mL/μm. Perhaps surprisingly, the role of this evolved gas seems not to have been considered. The polishing rate (surface recession rate) is empirically a few micrometers per minute, increasing with temperature, though there appears to be no published rate study as such in the modern parameter range.

Since the RF electromagnetic field penetrates only a thin surface layer of ~60 nm for niobium at a frequency of 1500 MHz [43], the chemical composition and topography of this layer is most important for RF performance. Elemental analysis [43], especially the composition of oxide layer and its contribution to surface resistance after BCP, have been studied [54] [76] [92] [93].

The BCP-polished surface displays a characteristic roughness with dramatic height variation and sharp edges , in contrast with the absence of optically visible topography after EP [76]. Crystal orientation and mechanical deformation can also affect surface roughness [77] after BCP. The similarity of feature size to the grain size, and the modestly faceted appearance have led some investigators to conclude that different etch rates on different crystal faces are responsible. No actual measurements of crystallite orientation versus polishing rate have been presented, however. Traditionally, the etched topography has been characterized in terms of a single parameter, typically a roughness number (e.g., R_q), with values in the few-μm range. R_q is not sufficiently incisive since

this value gives only the average of height variation but no information about sharpness of the features on the surface, and therefore the power spectral density (PSD) method was introduced [74]. PSD analysis reveals that the sharp-edged features characteristic of BCP develop by the first 10 μm removal from a nanopolished polycrystalline surface and that they are transformed into a characteristic rounded topography by the removal of a further 10 μm by EP [75]. Rate measurements may therefore be expected to show an initial transient on this scale and then a steady value encompassing nearly all further removal.

2.1.3. Goal of this study

The goal of the present study is to understand the genesis of topography in BCP with the ultimate aim of finding a path to surface smoothness comparable to that obtained by EP.

2.2. Experiments

The experiments aim to accurately measure polishing rate, to discover the impact of gas generation and to reveal the association of polishing rate with crystal orientation.

2.2.1. Materials

All the materials were from the sheet used for cavity production. Most were the standard 3 mm thick sheet having a grain size in the 50 μm – 100 μm range (“fine grained”). We also took advantage of the availability of large-grained (several cm) niobium to cut some single crystals and bi-crystals at the grain boundary.

2.2.2. Static polishing rate experiments

Samples were 10 x 10 x 3 mm³ squares. After electrical discharge machining (EDM) the samples were degreased and given a light (1-2 min) BCP etch to produce a uniform surface state, followed by rinsing with de-ionized water and air drying.

The static polishing rate experiments of fine grain samples were performed in a plastic beaker containing a freshly mixed 100 milliliter solution of HF (49%): HNO₃ (69%): H₃PO₄ (85%) at volume ratio of 1:1:2. A surrounding water bath was used to adjust the acid to the required temperature before each experiment. The temperatures were 0, 10, 20 and 30°C. A group of six fine-grain niobium samples were put in a Teflon basket and placed in the acid together. After 1, 2, 4, 6, 8 or 10 minutes, individual samples were taken out sequentially, rinsed immediately with de-ionized water and air dried. Weight and dimensions of the samples were measured before and after treatment. The polishing rate was calculated from weight loss divided by surface area, treatment time and density of niobium. Surface area before polishing was used for the rate calculation of polishing rate, assuming that the change of surface area is very small compared with initial or finishing surface area. As discussed later, in no experiment was the consumption of HF sufficient to bring about a meaningful difference in concentration between the beginning and the end.

For single crystal samples, a holder was used to ensure that each of the four samples has only one surface exposed to the acid. Ten steps of etching were carried out with the four samples placed vertically. The first five steps had duration of 6 minutes each, and the second five steps had duration of 12 minutes each. A total thickness about 120 µm was removed. These parameters were chosen to achieve total removal and topography in the range of production BCP.

The complex shape of real cavities assures that, in the BCP process, portions of the surface are present at a wide range of orientations. Different removal rates for segments facing different directions might result. For example, more rapid drainage of a surface film in the case a vertically positioned sample may bring about a higher removal rate than for a horizontally positioned facing-up sample. To explore this notion, we used a fixture to hold the samples so that their normal was pointing to three directions (up, down, and horizontal) during BCP, and their removal rates were measured. Figure 2.1 shows the experimental setup of samples with different orientation during BCP. Prior to treatment they were polished to a shiny, mirror-like surface to facilitate the observation of changes induced by BCP. Samples were polished for 6 minutes at 20°C.

2.2.3. Rotating polishing rate experiments

To study the influence of flow rate on polishing rate, rotating BCP was conducted at several speeds. Polycrystalline square samples with dimensions of 10 x 10 x 3 mm³ were weighed and inserted into the Teflon holder described in Figure 2.1. For each sample only one surface with an area of 10 x 10 mm² was exposed and all the other five surfaces were wrapped with Teflon tape. Therefore only one surface was polished during BCP. Three orientations of the etching surface were selected: facing up, facing down and facing horizontally. The Teflon sample holder was mounted to one end of a Teflon rod. The other end of the rod was mounted to a motor to enable rotating of the samples during BCP. The motor was clamped to an iron stand so that the rod was positioned vertically and the sample holder was horizontal and looked like a propeller. 250 ml room temperature (about 20°C) freshly made BCP solution with a volume ratio of HF (49%):HNO₃ (69.5%):H₃PO₄ (85%) = 1:1:2 was added to a plastic beaker. The rotating

speed was adjusted to required value through an external power supply before immersing the samples into the solution. Rotating speed we covered in this study was 0, 1, 12 and 60 rpm. The calculated surface speeds are shown in Table 2.1. After BCP for 6 minutes, samples were taken out of the acid and rinsed with de-ionized water thoroughly. Then samples were dried in the air and weighed again. We chose 6 minutes as BCP duration based on the static etching rate study results. The polishing rate vs. time curve drops exponentially at the beginning and seems to reach a plateau after 6 minutes. Removal rate was calculated from weight loss, etching time and etched surface area. For the purpose of topography observation, some samples were mechanically polished down to $0.1\ \mu\text{m}$ with polishing paper to a shiny surface, and then etched in the same process as the samples with light BCP-cleaned starting surface.

Figure 2.7. Experimental setup of BCP with different sample orientations

Table 2.2. Surface speeds of samples facing different direction at different rotating speeds

	1 rpm	12 rpm	60 rpm

Facing up	2.3 ~ 3.4 mm/s	27.6 ~ 40.2 mm/s	138.2 ~ 201.1 mm/s
Facing down	2.3 ~ 3.4 mm/s	27.6 ~ 40.2 mm/s	138.2 ~ 201.1 mm/s
Facing horizontally	3.9 mm/s	46.5 mm/s	232.5 mm/s

2.2.4. Temperature monitoring during BCP

In order to monitor the evolution of niobium temperature versus time through a BCP process, we prepared a rectangular polycrystalline niobium piece with dimensions of 11.2 x 33.8 x 3.3 mm³. A hole of 10 mm depth and 1.06 mm diameter was drilled from one end of this piece along the longitude direction for insertion of thermo couple. The sample was weighed before etching. A type T thermocouple was inserted into the sample. The data from the thermocouple was recorded by a computer at a rate of 1 per second. The acid temperature was measured with another thermocouple as a comparison. 100 ml 1:1:2 BCP acid was added into a small plastic beaker at room temperature (about 20°C). The sample was immersed into the acid with a length of 25.7 mm exposed to the solution. The temperature was monitored during BCP under different etching conditions such as static, external stirring, and sample rotating. For external stirring the speed ranged from 60 rpm to 180 rpm. For sample rotating the speed varied from 10 rpm to 180 rpm. After polishing for 6 minutes the sample was taken out of the acid, rinsed thoroughly with de-ionized water, air dried and weighed. Removal rate was also obtained from weight loss, polishing time and polishing surface area.

2.2.5. Topography study

Topography study was done on fine grain (polycrystalline), bi-crystal, and single crystal niobium. For fine grain niobium, temperatures were limited to 10°C and 22°C and polishing times were 1, 3, 7, 14, and 20 minutes. A group of specimens were mounted and polished metallographically to obtain nm-scale surface smoothness on one face (“nanopolished”). After dismounting by thermal shock, they were only rinsed with reagent grade isopropanol and air-dried. The nanopolished polycrystalline samples were polished in 1:1:2 BCP acid at room temperature for 6 minutes without agitation. The nanopolished bi-crystals and single crystals were polished at 20°C for 12 minutes (~30 μm removed) and subsequently another 80 μm removed for topography study. The polycrystalline samples with different orientations from polishing rate experiments were also subject to topography study.

2.2.6. Characterization

Surface topography of the samples was examined by optical microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM). Optical microscopy images were obtained on HIROX KH-7700 High Resolution Digital-Video Microscopy System. SEM was done on a Phenom G2 Pro desktop SEM. AFM data were collected with a Digital Instruments Nanoscope IV in intermittent contact (“tapping”) mode with a tip frequency of 300 kHz and a scan rate of 0.5 Hz. The AFM images correspond to a 70 μm x 70 μm area on sample surface.

Crystallite orientation of the polycrystal and bi-crystal samples was examined with electron backscatter diffraction (EBSD), primarily using an EDAX Pegasus XM4 on a FEI Helios 600 NanoLab at Virginia Tech.

2.3. Results

2.3.1. Polishing rate of fine grain niobium at different temperatures

In the BCP process, HNO_3 is the oxidizing agent that changes niobium from metal to pentoxide. HF is the dissolving agent that removes the niobium oxide formed on the surface of the metal, so that oxidization can continue. During polishing, brownish vapor came out of the solution, indicating NO_2 is generated. The reaction is often summarized as:

This means every mole of niobium removal yields 5 moles of NO_2 gas. The bath composition at the end consists of water-soluble H_2NbOF_5 and unreacted acid, ideally. As noted earlier, Malloch et al. [91] summarize the reaction differently, with NO rather than NO_2 as the gaseous product.

Figure 2.2 shows the measured polishing rate at 0, 10, 20 and 30°C. Each data point is the average value of three samples. The plotted rates are cumulative values over time, calculated by dividing the total weight loss by total amount of polishing time. Therefore each point reflects the result of the entire duration when the sample was in the solution. For each temperature, the rate started high, dropped gradually with time and reached steady-state at about 6 minutes. For the same duration of BCP, the rate increases with temperature from 0 to 20°C. The rate at 30°C started higher than 20°C at 1 minute, but fell to below 20°C after 2 minutes.

Figure 2.8. Polishing rate of poly crystal niobium as a function of polishing time for BCP at different temperatures

The observations above indicate that niobium BCP is a reaction with positive temperature dependence, so that the trend of polishing rate is understandable. At this point we take note of a very early [41] study of BCP polishing in the 20 – 50°C temperature range, reporting a rate of about 20 μm/min, independent of temperature. We return to this later.

At the beginning of polishing, acid reacts with the outermost surface layer of the samples. Having the highest density of defects and work damage within this layer, the reaction rate is often higher in this region [41]. As polishing continues to greater depth where the material is more uniform with less work damage, the reaction rate will slow down and reach a plateau. The law of the mass action says the reaction rate is proportional to the product of reactants' concentrations. The rate may be described by power law kinetics: $\text{Rate} = k[\text{HNO}_3]^a[\text{HF}]^b$, where k is the rate constant, $[\text{HNO}_3]$ and

[HF] represent the concentration of HNO₃ and HF at reaction site. Since our concentrations were effectively constant, the bracketed terms may be combined with k.

Fitting of the polishing rate vs. polishing time shows that the curve obeys a power law. Fitting parameters are shown in Table 2.2, with the equation:

$$Rate = k \cdot t^d$$

where Rate and t correspond to the average polishing rate of niobium and the polishing time t respectively, k and d are fitting constants. The quality of the fitting is good according to the R square value in Table 2.2.

Table 2.3. Fitting result for polishing rate vs. polishing time curve

Temperature °C	k	d	R ²
0	0.81	-0.25	0.95
10	1.70	-0.23	0.91
20	3.34	-0.16	0.91
30	3.36	-0.24	0.95

The shape of the curves looks very similar to each other, indicating that similar process happens at all these BCP runs. Temperature seems to affect the starting point of these curves and how quickly the polishing rate decreases.

2.3.2. Polishing rate of fine grain niobium with different orientations

The sample orientation affects the polishing rate significantly. The polishing rate at six minutes increased in the order of facing up 1.55 µm/min, facing down 2.7 µm/min, and facing hotizontally 2.9 µm/min, at 20°C. The etching rate was almost halved when

sample was facing up, inviting speculation that reaction product accumulates more extensively, reducing the rate.

2.3.3. Polishing of fine grain niobium under different agitating conditions

We investigated different ways to enhance surface flow on niobium during BCP process, and compared their effects in terms of etching rate versus static BCP. Stirring was done by moving a Teflon rod in the solution near the sample in a circular way, with the speed varying from 60 rpm to 180 rpm. Rotating was done by moving the sample directly in a circular way at speeds ranging from 10 rpm to 180 rpm. During agitated BCP, the temperature of the niobium was recorded with a thermocouple inserted into the sample. Figure 2.3 compares the results of removal rate under different agitating conditions. Figure 2.4 shows the fitting of removal rate as a function of rotating speed. Figure 2.5 shows the temperature-time curve corresponding to each agitating condition in Figure 2.3.

Generally speaking, for the same etching duration of 6 minutes, the removal rate was larger with agitation than without agitation. Static BCP was done twice: the first run had a removal rate of 1.9 $\mu\text{m}/\text{min}$; and the second run had a lower rate due to lower polishing temperature, as shown in Figure 2.5, since we have already shown that BCP etching rate increases with temperature. With stirring at 180 rpm, removal rate reached 3.0 $\mu\text{m}/\text{min}$, a 60% increase. When rotating the sample at 180 rpm, removal rate increased to 4.1 $\mu\text{m}/\text{min}$, more than doubled the static rate. At 60 rpm, stirring had a removal rate of 2.0 $\mu\text{m}/\text{min}$, while rotating sample had a removal rate of 2.9 $\mu\text{m}/\text{min}$. Rotating at 30 rpm and 10 rpm even showed higher removal rates than stirring at 60 rpm. All indicated that

rotating increased the etching rate more than stirring given the same agitating speed. The efficiency of stirring depends on the shape of the stirring tool and the location of stirring. The closer it is to the etching surface, the more effective the agitation will be. If stirring happens far from the reaction surface, the metal/solution interface can hardly feel the agitation distance away.

For the rotating agitation in this study, an exponential function fits the removal rate vs. rotating speed curve reasonably well. The polishing rate as a function of agitation rate can be expressed as $y = 2.6 \cdot e^{0.0025x}$, and the quality of the fitting R square is 0.97. This indicates that mass transfer also plays a role in the BCP process at room temperature.

We expect the removal rate at 30 rpm to be higher than that of 10 rpm, but the experiment result was the opposite. This again may be attributed to the lower temperature (~4 °C lower) of niobium sample during the 30 rpm run, as shown in Figure 2.5. The influence from the temperature seems more significant than from the flow rate in this case. In our experiment setup, keeping the acid temperature the same for each run was not easily achieved, and therefore the effect from flow and temperature were entangled. But the optimistic side is that we have two parameters to control the removal rate.

Figure 2.9. Removal rate of niobium after BCP under different agitating conditions, room temperature

Figure 2.10. Removal rate as a function of agitation strength represented by rotating speed

Figure 2.11. Temperature development of niobium during 6 minute BCP.

The BCP process is known to be exothermal so that both the niobium and the acid are heated up quickly. During the BCP of SRF cavities, agitation is usually applied by stirring the solution, shaking the cavity in the solution, or applying circulated etching solution. In this case, the agitation also helps prevent overheating by reducing the temperature difference between the reaction interface and the bulk solution.

2.3.4. Polishing rate with different orientations and rotating speeds

In real cavity BCP process, due to the shape of most cavities, the surfaces to be etched are oriented variously rather than simply in one direction as a flat sample does. For a mass transfer controlled process this can result in different removal rate for surfaces

facing different directions. For example, with the help of gravity, a vertically positioned sample may have higher removal rate than a horizontally positioned facing-up sample. This difference in etching rate may cause non-uniform wall thickness and even change the performance of cavities. To explore this speculation, we faced our samples in three directions during BCP and measured their removal rates. Considering that BCP for cavity production is usually conducted with circulating solution, we included the additional effect of agitation in our experiments as well. Figure 2.6 shows the average removal rate of 6 minutes BCP at room temperature, with samples facing the three directions and rotating at different speeds.

Two ways of surface preparation were used before conducting the etching rate study: light BCP (5~10 μm removed) cleaning and mechanical polishing. The mechanical polished samples had a shiny mirror-like surface. A smooth and uniform starting surface was expected to facilitate the observation of changes induced by BCP. Comparing the two sets of data in Figure 2.6, there were some fluctuations on the etching rate for the two types of samples treated under the same condition. But no significant difference was noticed, and there was no obvious indication that one had higher removal rate than the other.

Regardless of rotating speed during BCP, etching rate increased in the order of: facing up, facing down and facing horizontally. For static BCP, etching rate difference between facing up and the other two were significant, while the difference between the other two was small. For slow rotating at 1 rpm, the etching rate differences were distributed evenly among these three. For faster rotating from 12 rpm to 60 rpm,

horizontal-facing BCP had much higher etching rate than the other two, while facing down has a slightly higher etching rate than facing up.

Figure 2.12. Average etching rate of niobium after 6 minutes BCP at room temperature, facing three directions, rotating at 0 – 60 rpm: (A) Starting from light BCP cleaned surface; (B) starting from mechanical polished surface.

Apparently, rotating the samples increased etching rates for all three facing directions. Within the range of 0-60 rpm, the higher the rotating speed, the higher the etching rate was. Figure 2.7 shows the curves etching rate as a function of rotating speed for each direction. The starting curvature of the curves shows a bit difference for the three directions. At higher rotating speed, the curves have almost the same slope.

We noticed that the etching rate for vertical BCP in this set of experiments were higher than the value in previous results in Figure 2.3. This could be caused by: 1) starting surface condition. Light BCP and mechanically polished surface were used for Figure 2.7, while heavy BCP surface was used for Figure 2.3; 2) a larger beaker used in this experiment than in former experiment. The larger radius of rotation during BCP increased the velocity of the sample moving in the solution; 3) Figure 2.3 was obtained by manual stirring or rotating, therefore the speed can fluctuate during the process.

It is necessary to mention that in the BCP set up, horizontal-facing samples were placed a bit further from the rotating axis compared with the two vertical-facing samples. This resulted in higher moving speed on horizontal-facing samples.

Figure 2.13. Etching rate of niobium BCP at room temperature as a function of rotating speed, with different facing directions. Dark blue diamond: facing-up, light BCP surface. Red square: facing-up, mechanically polished surface. Green triangle: facing-down, light BCP surface. Purple cross: facing-down, mechanically polished surface. Light blue star: facing-horizontally, light BCP surface. Orange dot: facing-horizontally, mechanically polished surface.

2.3.5. Topography

Figure 2.8 below shows a polycrystalline niobium sample BCP treated at 20°C for 6 minutes, removing about 15 μm from the surface. It shows typical topography of the near-surface layer. Many individual grains can be identified. They appear to have been polished to different depths and are profusely pock-marked. Their appearance in optical images is termed “orange peel” and is widely recognized in metallography.

Figure 2.14. SEM image of typical polycrystalline niobium surface after BCP at 20 °C for 6 minutes

A five-fold higher magnification image (Figure 2.9) of a single grain shows that it is mostly surrounded sidewalls a few μm high. These are ridge or step shaped grain

boundaries reported previously [43] [55] [57]. The profile of the intersection of the pockmarks with the sidewall indicates that they are depressions, not protrusions. The grain interior exhibits small step-like features. It is not a smooth plane receding into the bulk as polishing continues. Note that these observations apply to the near-surface region.

Figure 2.15. SEM image of a close look at a single grain from Figure 2.8.

2.3.5.1. Influence of acid temperature on fine grain niobium topography

Figure 2.10 shows niobium surface topography after BCP at 22°C for different durations. The samples were fine grain niobium. And the polishing was done at static solution (only tilting the beaker occasionally to help the reaction product move away from niobium surface) with samples facing up. After one minute of polishing, the surface was dominated by small, concentrated protrusions possibly resulting from mechanical machining. As polishing continues, the surface smoothness improved by showing larger smooth regions. Plateau like features developed on the surface after seven minutes, although some detailed rough features still remained. The surface separated into smooth regions with different elevations and the area of each smooth region grew bigger as polishing continued. After twenty minutes of polishing, the surface was composed of large smooth facets with ridges and steps between each other, with few detailed features as found at the beginning. Note that all removals are significantly less than the grain size.

(A) M11 (22°C 1min; ~ 3 μm removal)

(B) M12 (22°C 3min, ~ 8 μm removal)

(C) M13 (22°C 7min, ~ 15 μm removal)

Figure 2.16. Optical microscope images of niobium after BCP at 22°C for: (A) 1 minute; (B) 3 minutes; (C) 7 minutes.

Figure 2.11 shows topography of niobium after BCP at 10°C for different durations. Characteristic features are similar to BCP surface at 22°C. Features develop more slowly

than at 22°C. We can see that BCP surface after 7 minutes at 10°C looks like the surface BCP treated at 22°C for a shorter time than 7 minutes.

(A) M20 (10°C 1min, ~ 2 μm removal)

(B) M22 (10°C 7min, ~ 7 μm removal)

(C) M24 (10°C 20min, ~ 20 μm removal)

Figure 2.17. Optical microscope images of niobium after BCP at 10°C for: (A) 1 minute; (B) 7 minutes; (C) 20 minutes.

Comparisons between the topographies of niobium polished at 22°C and 10°C showed consistent trends with regards to amount of removal. Higher temperature increased polishing rate so that given features appeared at earlier time than at lower temperature. Specimens having equal amount of material removal showed similar features, even though time and temperature were different, indicating that polishing mechanism is the same at these two temperatures. The results showed that the quality of polishing did not depend on etching temperature, as the samples etched at 10°C BCP did not show better (smoother) topography than those at 22°C. Only the mass removal mattered in determining the surface character.

2.3.5.2. Bi-crystal and single crystal niobium BCP topography

Gas evolution from the surface being polished caused by chemical reaction is a feature distinguishing BCP from other cavity polishing techniques. Figure 2.12 shows the print left by gas evolution during BCP, observed with optical microscope (A), SEM (B) and AFM (C). Without the influence of grain boundaries we can see clearly how gas evolution during BCP affects the surface: bubble prints appear. Bubble generation sites are not preferentially located at grain boundaries nor do grain boundaries (if present) appear to affect the development of bubbles. The large bubbles have a radius about 50 μm and a depth around 1 μm . Some bubbles evolve from the same spot, leaving the print of a series of concentric circles. Considering the forming of these crater shaped bubble prints, one hypothesis is that they are caused by poor heat transfer beneath the bubble at the generating site. When the bubble is growing on the surface, the surface adjacent liquid layer underneath cannot circulate with bulk solution and the temperature of this

layer increases. Therefore the area under the bubble is etched faster than area around it until the liquid layer is consumed. A close look by AFM at one bubble print is shown in Figure 2.12 (C). The print is flat at the bottom, slightly curved on the edge and has a depth about 1 μm . The diameter of the prints can vary between tens of micrometers and a hundred micrometers.

(A) B1.2 Optical microscopy

(B) B1.2 SEM

Figure 2.18. Surface morphology of Bi-crystal niobium after BCP at 20°C for 12 minutes: (A) Optical microscope image; (B) SEM image; (C) AFM image.

Note that some of the edges of these bubble prints show some sharpness and steps, especially where two bubbles meet. The gas evolution may contribute to the sharp features on the BCP surface of poly crystal samples although it cannot be seen clearly due to the confounding influence of many grain boundaries.

In the polished bi-crystals, a slight step is visible at grain boundary, but not as pronounced as maybe expected (Figure 2.12 (B) above). Further, no grain boundary grooving or other attack is evident here or in any other images. EBSD examination of the surfaces did not show coincidence with any of the cardinal orientations, see Figure 2.13. The two colors dividing up the square on the left correspond to two orientations. Referring to the color coded map on the top right corner, the position of the two colors tells the orientation of this bi-crystal sample lies in the blue and green area. The two dots

in the inverse pole figure on the lower right corner tell the exact position of the two colors. The mis-orientation angle between these two region is only 10 ~ 13 degrees. Therefore the polishing rate of the two grains may not be showing significant difference since their orientations are not very different from each other. Note that the grain boundary as such is not attacked.

Figure 2.19. Orientation of bi-crystal niobium (B 1.3) obtained by EBSD

Figure 2.14 (B)-(E) shows SEM images of the niobium single crystals after 90 minutes polishing. Again, all surfaces at lower magnification were covered by different shaped features on different single crystals. The orientations of the four single crystals we studied are shown in Figure 2.14 (A). One of them had a (101) surface, while the other three did not fall exactly at the corners in the inverse pole figure. Three of them were close to each other. Therefore the difference between patterns was not dramatic. In fact,

the polishing rate of these four single crystals did not show large variation either, about $1.8 \pm 0.2 \text{ } \mu\text{m/min}$ without a clear trend of removal rate order. At lower magnification, the saw-cut ridges on the samples before BCP persisted even after this much BCP, indicating that BCP does not level macro roughness efficiently. The surface looked increasingly smoother with increasing magnification, indeed almost featureless at 2000 magnification, the highest we conducted. Evidently in the absence of grain boundaries, BCP polishes well. The RMS roughness from AFM scan on an area of $50 \text{ } \mu\text{m} \times 50 \text{ } \mu\text{m}$ varied from 30 nm to 95 nm. Sample 1 and sample 4 showed slightly higher RMS than the other two samples. This is similar to the findings by D. Baars, et al. [77].

[001]

(A)

(B) K8

(C) K13

(D) K18

(E) K19

Figure 2.20. (A) Orientation of single crystal niobium samples used in this study, from EBSD analysis (1-K8, 2-K13, 3-K18, 4-K19); (B)-(E) SEM images of the four single crystal niobium samples in (A) after BCP at 22°C for a total of 90 minutes, removing an estimated 120 μm ; (F) RMS roughness of the four single crystal niobium obtained by AFM

2.3.5.3. Influence of crystal orientation on BCP topography

Seeking to reveal any variation of polishing rate for (001), (101) and (111) surfaces, we matched EBSD images and optical images of the same area and located two or three adjoining grains with these orientations (Figure 2.15). Using HIROX KH-7700 High Resolution Digital-Video Microscopy System with high magnification and multi-focusing technique, a close up 3D image of the surface was obtained. The height difference between these two grains was obtained by analyzing the profile of a line across two grains of interest (Figure 2.16).

Figure 2.15 shows the optical image of a polycrystalline niobium sample after 6 minutes of BCP at room temperature. Total removal was about 15 μm , which was small compared to the average size of a grain in polycrystalline niobium. The starting surface was nano-polished to a very low RMS roughness of a few nanometers. Therefore, we can relate the height variation after BCP to etching rate. An orientation map of a square area was obtained and overlapped onto the optical image of the same area. The color code is the same as in Figure 2.13. We were able to zoom in at a smaller area containing all three orientations of (100), (110) and (111), and successfully obtained the three dimensional profile of the surface by AFM, as shown in Figure 2.16. Here, the red lines on the image are the AFM traces presented below. The green lines mark the ends of each trace. As we expected different orientations would have different etching rates, we inspected the relative height of these three orientations and did notice there was difference on the micrometer scale. The profile in Figure 2.16 is a higher magnification optical image of the area within the dashed line box in Figure 2.15, comparing height difference between: (B) (111) to (101), (C) (111) to (001), (D) (001) to (101), we observe that (111) surface is about 2 μm higher (less material removed) than (101) surface, and (111) surface is about 1 μm higher than (001) surface. A similar trend was found at other places as well, even though the height difference may have some variation and the surface within a grain is not perfectly flat due to the influence from gas evolution or grain boundary effect. The height differences among these three major orientations are shown in Figure 2.17. The result may be summarized as: the polishing rate decreases in the order of (101), (001), and (111). D. Baars et al. [77] found that surface roughness of single crystal niobium after BCP is affected by crystal orientation and pre-existing mechanical

deformation. However, their study did not mention the polishing rate of different crystal orientations. According to our study, the 1~2 μm height difference resulted from 6 minutes of room temperature BCP means the removal rate difference is about 0.2~0.3 $\mu\text{m}/\text{min}$.

Figure 2.21. Optical microscope image of polycrystalline niobium BCP treated for 6 minutes at room temperature. The starting surface was nano-polished. The colored square is the EBSD image of the same area matched according to the grains. The area within the dashed box is magnified in Figure 2.16.

(A)

(B)

(C)

Figure 2.22. Optical microscope image of polycrystalline niobium after 6 minute BCP at room temperature, x1500 (A), and surface profile between different grains: (B) (111) to (101); (C) (111) to (001); (D) (001) to (101).

Figure 2.23. Average height differences among three major orientations of niobium after 6 minutes BCP at room temperature, sampled five to six spots for each column. The first index is the less-etched surface.

2.3.5.4. Influence of sample orientation on fine grain niobium BCP topography

Figure 2.18 shows optical and SEM images of fine grain niobium samples BCP treated at 20°C for 6 minutes, with samples facing up, facing down and horizontally.

There was no evident effect of sample orientation on topography at small scale. However, bubbles were easily trapped on the surface when the sample was facing down, while the other two directions had hardly any bubble prints left on the surface.

(A) P32 (Up)

(B) P35 (Down)

(C) P37 (Vertical)

(D) P35 (down)

Figure 2.24. Optical and SEM images of mechanically polished polycrystalline niobium samples after 6 minutes BCP at room temperature. Samples were placed: (A) facing up; (B) facing down; (C) vertically. (D) shows the bubble prints at low and high magnifications.

2.4. Discussion

2.4.1. Temperature dependence of BCP polishing rates: Arrhenius equation

As an experimental finding, the Arrhenius equation describes the relation between reaction rate constant k , activation energy E_a and temperature T [94]:

$$k = A \cdot \exp(-E_a/RT)$$

where A is the pre-exponential factor, R is the gas constant. For most chemical reactions, this equation works well over a limited temperature range. Even in a complicated multi-step reaction the Arrhenius equation can be used to describe the temperature dependence of the overall reaction rate.

Reaction rate constant k is temperature dependent. For a set temperature, k remains constant, and the reaction rate is decided by the concentration of the reactants. As reaction noted earlier:

$$\text{Rate} = k \cdot [\text{HNO}_3]^a \cdot [\text{HF}]^b$$

$$\begin{aligned}\ln \text{Rate} &= \ln(k \cdot [\text{HNO}_3]^a \cdot [\text{HF}]^b) = \ln(A \cdot \exp(-E_a/RT) \cdot [\text{HNO}_3]^a \cdot [\text{HF}]^b) \\ &= \ln A + \ln([\text{HNO}_3]^a \cdot [\text{HF}]^b) - E_a/RT\end{aligned}$$

If plotting of the natural logarithm of the reaction rate versus temperature reciprocal $1/T$ follows a straight line for certain temperature range, the activation energy can be determined from the slope:

$$E_a = -\text{Slope} \cdot R$$

Knowing the activation energy for a reaction helps to decide whether the process is controlled by chemical reaction or diffusion [95]. The intercept on rate axis, $\ln A +$

$\ln([\text{HNO}_3]^a \cdot [\text{HF}]^b)$, can be considered as constant if $[\text{HNO}_3]$ and $[\text{HF}]$ remain constant. Constant composition is a reasonable approximation here, since in 100 ml fresh BCP solution the amount of HF is about 0.7 mol. The largest removal of niobium we had in one run was 0.26 g, which consumed only 0.014 mol HF. Therefore bulk concentration of HNO_3 and HF can be considered as constant, since the amount of acid is much larger than niobium. Knowing that the beginning rate of the reaction is transient due to the damage layer, we use the reaction rate at the sixth minute of each run where the rate enters a plateau, with the assumption that the acid concentration is still the same. Here we also assumed that the volatilization of HF is very small as we are not running at high temperature.

Figure 2.19 shows the logarithm of polishing rate as a function of temperature. The composition of the solution is the same at the beginning of each run; therefore we can ignore the influence of the other parameters, i.e. acid concentration, product concentration, so that temperature is the only parameter that changes.

Figure 2.25. Logarithm of the polishing rate ($\ln(\mu\text{m}/\text{min})$) as a function of the reciprocal of temperature ($1/\text{Kelvin}$) from 0°C to 30°C .

The polishing rates in the plot are from the points of the sixth minute in Figure 2.2. Fitting reveals a well-defined linear relation between $\ln(\text{Rate})$ and $1/T$ from 0°C to 20°C . However, polishing rate at 30°C seems to deviate from this line and heading to a smaller slope. The work noted earlier [41] reported a regime from 30°C to 50°C in which the polishing rate is temperature independent. Similar observations have been reported for the etching processes of other materials [95], indicating that a high activation energy below 20°C and a low one above this temperature. We propose that between 20°C and 30°C is a divide between two different rate-limiting mechanisms. For temperature from 0°C to 20°C , the activation energy of the polishing reaction we studied is:

$$E_a = -\text{Slope} \cdot R = 6469.8 \times 1.986 \text{ cal}/(\text{K} \cdot \text{mol}) = 12.85 \text{ kcal/mol}$$

In general the activation energy for a diffusion limited process is less than that for a chemical reaction rate limited process, and it is not affected significantly by reactant

concentration. As a general guidance, the activation energies for diffusion are less than about 7 kcal/mol [95]. We therefore infer that from 0°C to 20°C polishing rate is likely to be chemical reaction controlled.

The intercept on y axis, $\ln A + \ln([\text{HNO}_3]^a \cdot [\text{HF}]^b)$, can be used to determine the value of A when the value of a and b are known.

One of the general criteria of a diffusion-controlled rate is: the temperature coefficient is in general less than 1.5 per 10°C [96]. The temperature coefficient within a certain range is defined as the ratio of the rate coefficients at the higher limit (k_2) and the lower limit (k_1) in our discussion. If the temperature coefficient is greater than 2.0 per 10°C the chemical reaction is slow and controls the observed rate [96]. In our study the temperature coefficient is listed in Table 2.3.

Table 2.4. Temperature coefficient of BCP reaction at different temperature ranges

Temperature range	Temperature coefficient (k_2/k_1)
0-10 °C	2.24
10-20 °C	2.25
20-30 °C	0.84

The temperature coefficient from 0 °C to 10 °C is 2.24, in the range of chemical reaction control. From 10 °C to 20 °C, it stays the same at 2.25. From 20 °C to 30 °C, it reduces to 0.84. The message is: as the temperature increases, the rate of chemical reaction step increases faster than the rate of mass transfer (diffusion, convection, etc.) does [96], and therefore mass transfer shows more influence on the removal rate.

2.4.2. Determining the order of BCP reaction from rate of reaction data

The rate law for the BCP reaction can be estimated from the polishing rate at different concentrations of the reactants, i.e. different percentages of HNO₃, HF and H₃PO₄.

For reaction:

$$\text{Rate} = k \cdot [\text{HNO}_3]^a \cdot [\text{HF}]^b$$

The rate depends on the concentration of HNO₃ and HF [94]. If we fix the concentration of one of these two acids, and compare the reaction rates at different concentrations of the other acid, we will be able to determine the value of a and b in the rate law above. We attempt to accomplish this by extracting data from a study done by V. Palmieri et al [97], Figure 2.20.

Figure 2.26. Curves of equal polishing rate (μm/min) versus different percentages of HF, HNO₃ and H₃PO₄, in the three-dimensional space of BCP [97].

To determine the value of b , we chose some points with the same HNO_3 proportion but different HF proportion. Two set of points were selected and listed in Table 2.4. Compare the reaction rate of the other four points with the first point, and the ratio is proportional to the [HF] ratio of each pair to the b^{th} power.

Table 2.5. Data extracted for determination of b

	HNO_3	HF	H_3PO_4	Rate of reaction ($\mu\text{m}/\text{min}$)	[HF] ratio	Rate ratio	b
Point 1	0.4	0.2	0.4	1			
Point 2	0.4	0.28	0.32	2	1.4	2	2.1
Point 3	0.4	0.36	0.24	4	1.8	4	2.4
Point 4	0.4	0.4	0.2	5	2	5	2.3
Point 5	0.3	0.1	0.6	0.1			
Point 6	0.3	0.3	0.4	2	3	20	2.7
Point 7	0.3	0.38	0.32	4	3.8	40	2.8

$$b = 2.4 \pm 0.3$$

Similarly, to determine the value of a , we select a few points with the same HF proportion but different HNO_3 proportion. Three sets of points were selected and listed in Table 2.5.

Table 2.6. Data extracted for determination of a

	HNO ₃	HF	H ₃ PO ₄	Rate of reaction (μm/min)	[HNO ₃] ratio	Rate ratio	a
Point 1	0.25	0.25	0.5	1			
Point 2	0.525	0.25	0.225	2	2.1	2	0.9
Point 3	0.44	0.35	0.21	4			
Point 4	0.53	0.35	0.12	5	1.2	1.25	1.2
Point 5	0.3	0.3	0.4	2			
Point 6	0.55	0.3	0.15	4	1.8	2	1.1
Point 7	0.625	0.3	0.075	5	2.1	2.5	1.2

$$a = 1.1 \pm 0.1$$

Since the influence of temperature on reaction rate is considered in k, we can assume that a and b are applicable in the temperature range of this study. Now we have the rate law looking like:

$$\text{Rate} = k \cdot [\text{HNO}_3]^{1.1} \cdot [\text{HF}]^{2.4}$$

Bringing it back to Arrhenius plot intercept, we have the value of A equals 1.1. With this rate equation, one can estimate the removal rate knowing the temperature, the activation energy, and the acid concentration.

2.5. Conclusion

We have investigated the genesis of topography in buffered chemical polishing of niobium for SRF accelerator cavities. Our major findings are:

For metal not previously etched, after removal of an initial few μm , the polishing rate is constant with time and increases with etchant temperature. The resulting topography depends on total removal, which can be adjusted by polishing time and etchant temperature.

Correlation of etch depth with crystallographic orientation indicates the order of rates to be $110 > 100 > 111$, with a rate difference $\sim 10\%$ of the average removal rate of BCP. For the bi-crystals with two grains similarly orientated, no evidence was found for strong differential etching and grain boundary attack.

The polishing process is controlled by the surface reaction(s) under 0°C to 20°C range. At 30°C , another regime appears, consistent with previous reports. Clear evidence was found for the impact of gas evolution on topography, especially when sample was facing downward in the solution. These findings apply to the 0°C to 20°C range, which encompasses current production practice.

This study indicates that the characteristic topography generated by BCP is inherent and fundamental. Our systematic analysis also yields the guidance that to avoid large roughness from BCP, lower temperature and solution agitation is preferred. In this way, a better control of the removal can be achieved and bubble prints on the surface can be avoided.

CHAPTER 3

Influence of surface flow on topography in electropolishing (EP) of niobium

3.1. Introduction

The previous chapter showed that the surface roughness produced by BCP is inherent to the nature of chemical etching. Limiting the total removal and reducing gas accumulation on the surface help to avoid large roughness, but there is not much could be done to eliminate the sharp features by varying BCP itself. When it comes to the final step of surface treatment where high gradient is required, BCP will not be the choice. EP is the most likely candidate, even if it has a polishing rate ten times slower than BCP. With an already satisfactory surface topography, our goal here is to find if there is a possibility to increase polishing rate within practical range.

3.1.1. Practice of EP on niobium cavities

The recipe for niobium EP used nowadays was developed in 1971 by Siemens [42]. They found that polishing is usually accompanied by a current oscillation on the current-time curve. The electropolished superconducting niobium cavity showed high Q_0 value and critical magnetic field [42]. It was also demonstrated by other groups that EP can improve cavity performance especially at high gradient [98]. Later, based on the

horizontal EP equipment developed by Siemens, K. Saito et al. [98] further implemented and simplified the EP process for superconducting cavities at KEK during the TRISTAN energy upgrade. They found that the current oscillation is not necessary for polishing and a horizontally rotating continuous EP system was developed. Their methods enabled mass production and reached gradient of ~ 40 MV/m for 1300 MHz single-cell cavities with a high probability.

Horizontal EP was developed and used in the early days of cavity EP. Currently horizontal EP setup is still used in KEK, DESY, JLab, FNAL/ANL and industrial companies like ZANON and RI [47]. Figure 3.1 is the horizontal EP setup at JLab and Figure 3.2 is the acid flow scheme of the horizontal EP system at ANL. Single cell or multi cell niobium cavities as anode are placed horizontally on a frame. An aluminum tube as cathode is inserted axially in the cavity. The electrolyte is usually a mixture of 49% HF and 96% H_2SO_4 in a volume ratio of 1:9. The acid enters from one end of the cathode and flows into the cavity through a few holes on the cathode wall. The cavity is filled up to 60% full with acid. It rotates about the longitudinal axis at a speed of 1 rpm during the polishing, so that the entire inner surface of the cavity is polished. Nitrogen flow is introduced above the acid inside the cavity to take away the hydrogen generated by the reaction. The acid comes out from the two ends of the cavity and flows back to the reservoir where the temperature of the acid is regulated. The acid circulation system helps maintain the acid temperature and establish flow between cavity and electrolyte. Traditionally, the applied voltage has been around 17 V and current 300 ± 20 A for a 9-cell cavity [36]. Start temperatures are typically 20 to 23°C, and the set point temperature could be 30-35 °C [36]. The removal rate is about 0.4 $\mu\text{m}/\text{min}$. Jefferson Lab developed

new insights into EP and achieved satisfactory performance from CEBAF 7-cell low loss cavities by applying a light EP process. In the light EP, the cavity wall temperature was kept at 20 °C and the removal varied between 10 μm and 40 μm [99]. When the polishing is finished, the power is turned off while circulation and rotation continue for 30 minutes to assure dissolution of remaining niobium oxide. The cavity is then put vertically to drain the acid. Then the cavity is thoroughly rinsed with ultrapure water and ethanol if needed. A mild bake at 100-130°C for 24~48 h is needed after EP [36] [99].

Figure 3.27. Jefferson Lab horizontal EP system [47]

Figure 3.28. Acid flow schematic for horizontal EP (courtesy of ANL) [36]

Vertical EP of niobium cavities has been developed at Cornell University (Figure 3.3), JLab, Saclay and KEK [47]. The cavity is positioned vertically and kept stationary during vertical EP. Since the cavity is not rotating, this setup is simpler than the horizontal EP system. At Cornell University, the cavity is filled with acid and agitation is done by stirring paddles attached to the cathode during polishing. At the end of polishing, the acid is drained from the bottom of the cavity. For vertical EP with circulating acid in JLab, the acid flow is similar to the circulating BCP setup, entering from the bottom and flowing out from the top. The generated hydrogen is brought out from the top. Having

similar uneven removal rate problem with the vertical BCP setup, flipping the cavity between two sessions of EP is needed for uniform material removal.

A

B

Figure 3.29. Vertical EP system at Cornell University: (A) schematic layout; (B) photograph of the setup [100]

3.1.2. Fundamentals of EP

Electropolishing (EP) is an electrolytic method to obtain a smooth, bright surface, discovered in the 1930's on copper [101]. The material to be polished is the anode. The anode and a counter electrode (the cathode) are immersed into a proper electrolyte and connected to a power supply to form a complete electric circuit. During polishing, the anode gives out electrons and the surface material is dissolved into the electrolyte. The polishing starts from smoothening at the micro scale, and extends to the macro scale with increasing removal amount. The anodic current increases with voltage as the voltage ramps up and reaches a plateau where the current does not change with voltage. When the voltage exceeds certain value, the current may increase again but different reactions may be involved. The limiting current plateau region on the anodic current-voltage curve is usually chosen as the polishing condition. Electropolishing is normally carried out in concentrated acid media such as phosphoric acid and sulfuric acid. Mass transport plays an important role in obtaining polishing [102]. Different transport mechanisms have been proposed regarding whether the rate-limiting species are the cations of the dissolving metal, or acceptor anions from the solution, or water from the solution.

The essential means of electropolishing is an electrolytic cell, as shown in Figure 3.4. For circumstances of present interest, niobium is the anode connected with the positive pole of the power supply, while aluminum is the cathode connected with the negative pole of the power supply. During polishing, electrons move away from niobium

under the electric potential difference provided by the power supply. Electrons at the cathode combine with H^+ from the electrolyte, and hydrogen gas evolves on the cathode. An oxide film is formed on the niobium and is dissolved by HF or HF_2^- from the electrolyte, allowing the reaction on the anode to continue. In the electrolyte, positive ions (cations) migrate towards the cathode and negative ions (anions) migrate towards the anode under the electric field. Thus a complete electric circuit is maintained. The steady state total current is regulated by the diffusion of fluorine species to the oxide film [63]. The principal reaction equation can be described as:

Anode [50]:

Cathode:

Figure 3.30. Schematics of an electrolytic cell with copper cathode [103]

The interface between electrode and electrolyte was first proposed to have a double layer structure by Helmholtz [103]. The charge distributed within the electrode and the

counter-charge from the electrolyte residing at the electrode surface forms a double layer structure. Later, the Gouy-Chapman-Stern (GCS) model was developed to better explain the capacitance behavior of the interface, where a diffuse layer of charge was introduced in the solution side. The layer closest to the electrode contains solvent molecules and some specifically adsorbed ions or molecules. The locus of the electrical center of the specifically adsorbed ions is called the inner Helmholtz plane (IHP). The locus of centers of nearest solvated ions is called the outer Helmholtz plane (OHP). The solvated ions distribute throughout the diffuse layer, which extends from the OHP into the bulk solution. The double-layer region is shown in Figure 3.5 [103].

Figure 3.31. Double-layer model of electrode/electrolyte interface according to GCS theory [103]

Both faradaic and nonfaradaic processes occur when electrode reactions take place. For nonfaradaic process, where no charge-transfer reaction occurs and charge cannot

cross the electrode-electrolyte interface, the behavior of the interface is analogous to that of a capacitor. For Faradaic process, electrons are transferred across the metal-solution interface causing oxidation or reduction. Such reactions are governed by Faraday's law and hence the name. The current (i)-potential (E) characteristic of this electrode reaction looks like that of a pure resistance. The rate of an electrode reaction is affected by electrode variables (material, surface area, geometry, surface condition), mass transfer variables (diffusion, convection, surface concentrations, adsorption), solution variables (bulk concentration of electroactive species, concentration of other species, solvent), external variables (temperature, pressure, time) and electrical variables (potential, current, electric charge). The electrode reaction can be represented by a series of resistances (or impedances) representing various steps. The potential difference defined by the power supply is distributed among the anode reaction, the cathode reaction, and the ohmic drop in the solution. A whole cell polarization curve (i - E) curve is obtained by applying a voltage across an electrolytic cell and measuring the current flowing through the cell. Due to the potential drop in the solution, most electrochemical experiments studying a working electrode (WE) use a three-electrode system (Figure 3.6), where the potential of the WE is monitored relative to a separate reference electrode (RE) positioned very close to the WE. A high input impedance device is used to measure the potential difference between the WE and the RE, so that the current through the RE can be neglected and its potential will remain equal to its open-circuit value.

Figure 3.32. Three electrode cell [103]

The average surface roughness can be lower than $0.5\ \mu\text{m}$ with EP [36]. EP produces a wavy but smooth topography without any sharp edges. The smoother surface finish is one obvious advantage of EP over BCP, which leads to better cavity performance at high gradient [61]. However, EP is unlikely to completely remove large defects pre-existing on the surface [104] [105]. The surface oxide layer of electropolished niobium has similar composition as that of chemically polished surface, consisting of a dielectric pentoxide (Nb_2O_5) layer on the outer most as majority and a thin lower oxide (such as NbO and Nb_2O) interlayer perhaps between Nb_2O_5 and the metal niobium, except that the Nb_2O_5 layer seems to be thicker for electropolished or anodized niobium [93]. The limiting current is sensitive to HF concentration in the electrolyte and the temperature near the niobium anode. The reaction mechanism studied by electrochemical impedance spectroscopy (EIS) shows evidence that EP of niobium with the standard electrolyte is a mass transport controlled process involving a compact salt film mechanism [63]. The diffusion layer thickness is found to be about $10\text{--}20\ \mu\text{m}$ within the temperature range of

1~50°C using rotating disk electrode (RDE) [87]. A study combining voltammetric, steady-state, and impedance methods can give further insight into the reaction mechanism of EP [106]. HF-free EP recipes are under development to reduce the usage of the hazardous acids [107] [108] [109] [64] [65].

3.1.3. Motivation of surface flow rate study of niobium EP

The flow rate of the electrolyte near the niobium surface is an important parameter in cavity EP. EP is a temperature and flow dependent process [63], especially during higher voltage EP. The limiting current is affected by the diffusion of reactive species. Agitation can change parameters that affect the diffusion process. These parameters include the thickness of the diffusion layer on the niobium surface, temperature distribution in the electrolyte and the transport of the reaction product on the electrodes, such as the hydrogen bubbles and niobium salts. Moderate agitation can help maintain the current oscillation (which may be beneficial but not necessary) by modulating the viscous layer thickness [36]. Hydrogen pickup by the cavity is another concern with EP [98] [110] [111]. Guiding hydrogen out of the system quickly can reduce hydrogen pickup and possible reaction between hydrogen and sulfuric acid. In horizontal EP the cavity rotation and the acid circulation produce the flow over the niobium surface. In vertical EP, the stirring paddles or the acid circulation produce the flow. Simulation of the hydrodynamic and thermal aspects during EP is helpful for optimizing polishing parameters [112]. K.Saito et. al. [110] found that rotating speeds between 1 and 3.5 rpm are good for 1.5 GHz single-cell cavities, and its effect on polished states is small when less than 10 rpm. In JLab 7-cell cavity horizontal EP process, fresh electrolyte is supplied at about 3 L/min into the cavity. The niobium cavity (anode) rotates at 1 rpm, corresponding to motion at

the equator of 1 cm/s [112] and at the iris of 4.2 cm/s for the ILC cavity geometry. Thus a flow circulation is formed inside the cavity and flow conditions vary significantly at different locations.

The purpose for this study is to further understand how the acid flow velocity affects surface topography and roughness at both macro scale and micro scale. Rotating speed of the samples is selected so that the whole present cavity processing range is covered. It is equivalent to a combined effect of cavity motion and electrolyte flow. We hope to understand and improve the surface topography resulting from EP under different flow conditions.

3.2. Experiments

3.2.1. Material and preparation

The niobium samples used for flow-EP study were high purity poly-crystal squares cut from RRR sheet material. The polishing area of each sample was 1.9 cm x 1.9 cm. The samples were buffered-chemical-polished (BCP) with the 1:1:2 recipe for 1 hour at room temperature (20 °C), removing about 150 μm from the surface. They were then ultrasonically rinsed with de-ionized water and air dried. The samples were then inserted into a Teflon holder and mounted vertically on a rotating Teflon disk for the polishing experiments (Figure 3.7). The distance between the center of the disk and the center of niobium sample was 3.5 cm.

3.2.2. Electrochemical cell setup and polishing experiments

About 800 ml fresh solution of HF (49%): H₂SO₄ (96%) = 1:10 (vol. %) was used as the electrolyte for each EP experiment. The electrolyte was contained in a Teflon beaker. A Teflon disk holding the niobium sample was placed horizontally covering the opening of the beaker. The samples were fully immersed in the electrolyte during the polishing. A high purity aluminum rod with a diameter of 1.27 cm was used as the cathode and vertically mounted at the center of the Teflon disk. During the polishing, the disk and the samples rotated along the aluminum rod at selected speeds, powered by a motor attached to the Al rod.

The voltage for EP was provided by a Sorensen DCS 33-33E power supply. The niobium to be polished was connected to the positive pole and the aluminum was connected to the negative pole. One niobium sample was polished at a time, and one niobium sample was used at each flow condition. The polishing was carried out for 90 minutes at a cell voltage of 14 V for each run. The polishing started at room temperature (20 °C) and finished at about 22 °C, removing about 40 μm from the surface of niobium. The rotating speed varied between 0 to 10 rpm, corresponding to surface flow rate of 0 ~ 3.7 cm/s assuming static fluid. Unlike real cavity processing, the niobium coupons were always immersed in the solution during EP in our experiments. The total current through the cell was recorded with a Keithley 2000 multimeter. Current-time (I-t) curves were recorded by a customized LabVIEW program.

3.2.3. Characterization

The surface topography before and after EP were obtained with optical microscopy (HIROX KH-7700 High Resolution Digital-Video Microscopy System), atomic force microscopy (AFM) (Digital Instruments Nanoscope IV), and surface profilometry. AFM

was done in tapping mode with silicon tips and the scan size was $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ for each image. Each AFM image consisted of 512 scan lines and there were 512 data points for each line. The root mean square (RMS) roughness was obtained from these AFM data. The power spectral density (PSD) analysis was done using the same method described in reference [74].

Figure 3.33. Sketch of rotating- electrode EP set-up

3.3. Results and discussion

3.3.1. Influence of flow rate on current-time curve and material removal

Figure 3.8 (A) presents the plots of the total current (I) going through the circuit as a function of polishing time (t). The I - t curves were collected at different surface flow rates. Figure 3.8 (B) is the steady state total current (I) as a function of different surface flow rates. At the beginning of EP, the transient current shows a peak and drops exponentially within the first 500~1000 seconds. Then the current reaches a plateau,

which means the polishing process has reached a steady state. The transient behavior can be understood as the consumption of the reacting species near the electrode and the establishment of a diffusion layer. The steady state current was around 0.125 A for static EP, and rose slightly to 0.14~0.16 A when the surface flow was increased to 0.7~3.7 cm/s. I-t curves indicated only a slight increase of polishing rate with flow rate within the range of this study.

Figure 3.34. Current-Time curve (A) and steady state current (B) at different surface flow rates from 0 to 3.7 cm/s

Figure 3.9 (A) shows the mass loss of niobium samples after EP at different flow rates. Only insignificant fluctuation of mass loss was observed for these flow rates. We calculated the amount of removal using data both from mass loss:

$$\Delta M(mol) = \frac{\Delta m(g)}{92.9(g/mol)}$$

and the total charge passed through the cell:

$$\Delta M(mol) = \frac{\int_0^t I(A)dt(s)}{96500(C/mol) \times 5}$$

as shown in Figure 3.9 (B). This is equivalent to ~48 μm of niobium removed from the surface. The results from these two methods confirmed that the removal rate was not significantly affected by the flow rate. This is helpful for interpreting variation in local

removal rates in niobium cavities and to what extent careful flow management is required to obtain uniform removal. Clearly it is not.

Figure 3.35. (A) Weight loss of Nb samples and (B) Calculated amount of Nb loss by current-time curve, after EP at different rotating speeds from 0 to 10 rpm, corresponding to surface flow rates from 0 to 3.7 cm/s

3.3.2. Influence of flow rate on surface roughness

Figure 3.10 (A) shows the average RMS roughness of three spots on each niobium sample measured by AFM and the roughness at the center of each sample measured by surface profilometer. For AFM, three spots were selected near the center of the sample, each having an area of $50\text{ }\mu\text{m}$ by $50\text{ }\mu\text{m}$. The average roughness R_q decreased from 80 nm for static EP to around 35 nm for EP under a flow rate of 3.7 cm/s. RMS roughness was improved slightly on this scale within the flow rate range we studied. Figure 3.10 (B) shows the RMS roughness obtained by profilometer, from an area of $500\text{ }\mu\text{m}$ by $500\text{ }\mu\text{m}$ at the center of the sample. No significant difference was found between rotating EP and static EP samples on this larger scale and the roughness of all the samples fluctuated slightly between $0.8\text{ }\mu\text{m}$ and $1\text{ }\mu\text{m}$.

Figure 3.36. RMS roughness (R_q) of niobium after EP at different surface flow rates (0, 2, 4, 6, 8, 10 rpm correspond to 0, 0.7, 1.5, 2.2, 2.9, 3.7 cm/s respectively), obtained by (A) AFM ($50\ \mu\text{m} \times 50\ \mu\text{m}$) and (B) surface profilometer ($500\ \mu\text{m} \times 500\ \mu\text{m}$)

Figure 3.11 shows the PSD analysis of niobium topography including the starting BCP surface and surfaces after EP at different flow rates. BCP surface with facets and sharp edges showed a linear trend. After EP, the sharp features were rounded and flat facets became wavy. Contribution from all spatial frequencies was reduced, especially that from high frequency. However, the topography difference resulted from EP at various flow rates was not distinguishable.

Figure 3.37. PSD analysis of niobium topography from the starting BCP surface to surface after EP at different flow rates. The PSD plots were calculated from AFM data.

3.3.3. Influence of flow rate on surface topography

Figure 3.12 shows the optical microscope and AFM images of niobium samples after static EP and some typical images after rotating EP. The area of the optical microscope image was about $320\ \mu\text{m} \times 240\ \mu\text{m}$ and the area of the AFM image was $50\ \mu\text{m} \times 50\ \mu\text{m}$. Images were all taken at the center of niobium samples. The optical images showed that the sharp edges on the surface were smoothed out by EP. And less surface unevenness was observed as flow rate increased. However, the changes were not significant. With a closer look by the AFM images, the surface was smoothed on micro scale.

A

B

Figure 3.38. (A) Spots where optical and AFM images were taken on Nb samples; (B) Topography of Nb samples before and after $\sim 50 \mu\text{m}$ EP (0, 2, 4, 6, 8, 10 rpm corresponding to static, 0.7, 1.5, 2.2, 2.9, 3.7 cm/s); left column: optical images of Nb samples with 1050 magnification; right column: AFM images of Nb samples with an area of $50 \mu\text{m} \times 50 \mu\text{m}$

We found that after rotating EP, the leading edge (the left edge in our study) of niobium samples had smaller waviness on macro scale (e.g. eyes and optical microscope), but has larger micro scale roughness under AFM, as shown in Figure 3.13.

RMS roughness obtained with AFM was 163 nm within 1 mm from the left edge and 48 nm at the center. This could be a combined effect of electric field and flow that changed the polishing effectiveness at the edge.

Figure 3.39. Topography at the leading edge comparing at the center of Nb sample after EP under 2.2 cm/s flow. The size of the optical images were $320 \mu\text{m} \times 240 \mu\text{m}$. The size of the AFM images were $50 \mu\text{m} \times 50 \mu\text{m}$. (A) AFM image on the left edge; (B) AFM image at the center; (C) Optical image on the left edge; (D) Optical image at the center

3.3.4. Influence of flow rate on diffusion layer

In static EP, the convection is mainly from the natural movement of the electrolyte due to density and temperature differences, and this does not significantly change the thickness of gradient layer of fluorine (the etchant). However, when the electrode is rotating during EP, convection introduced by flow cannot be ignored. A velocity boundary layer is formed near the surface of the niobium electrode due to the flow. The thickness of this velocity boundary layer is [113]:

$$\delta_B = 5\sqrt{\nu y/u_0} \quad (3.1)$$

Where: ν , coefficient of kinematic viscosity, $29 \text{ cP}/(1.76 \text{ g/cm}^3)=1.65\times 10^{-1} \text{ cm}^2/\text{s}$ for EP solution at 19°C [87]; u_0 , bulk velocity of electrolyte, here we select the tangential velocity at the center of the niobium samples, which is $0\sim 3.7 \text{ cm/s}$; y , distance from impact point (the leading edge). The flow rate $u=0$ at the surface of niobium, and $u=u_0$ outside the velocity boundary layer.

Inside the velocity boundary layer, very close to the Nb surface is the concentration boundary layer, whose thickness is δ . Within this concentration boundary layer, mass transport is mainly accomplished by diffusion. This concentration boundary layer is also called diffusion layer. Evidence was found that the diffusion of fluorine from bulk electrolyte to the surface of niobium is the rate-limiting step in EP process [63]. Therefore we expect a fluorine concentration gradient is formed within this region. The thickness of this diffusion layer can affect the limiting current during polishing. By applying forced convective flow near the electrode surface, such as a rotating disk electrode (RDE), the thickness of the diffusion layer can be change. Higher anode rotating speed results in higher polishing current. The thickness of the diffusion layer is

estimated to be tens of microns [87]. According to fluid dynamics and convective mass transfer theories [113], the relation between the thickness of the effective diffusion layer δ and the velocity boundary layer δ_B can be expressed as

$$\frac{\delta}{\delta_B} \approx \left(\frac{D_i}{\nu} \right)^{1/3} \quad (3.2)$$

Where: D_i , diffusion constant of fluorine.

To compare the influence of temperature and flow rate on mass transport, we calculated the velocity boundary layer and effective diffusion layer thickness at the center of niobium at different flow rates (0.7-3.7 cm/s) and temperatures (1-50 °C). The dynamic viscosity and diffusion coefficient used for calculation is from reference [87]. The result is shown in Figure 3.14.

Figure 3.40. (A) The thickness of the velocity boundary layer at the center of niobium during EP at different flow rates and temperatures; (B) The thickness of the effective diffusion layer at the center of niobium during EP at different flow rates and temperatures

Notice that the dynamic viscosity ν of the EP electrolyte decreases as temperature increases, while the diffusion coefficient δ increases with temperature. According to equation (3.2), the thickness of effective diffusion layer is proportional to $\nu^{1/6}$ and $D_i^{1/3}$, with D_i increasing with temperature and ν decreasing with temperature. According to equation (3.1), the thickness of boundary layer is only proportional to $\nu^{1/2}$, which decreases with temperature. Therefore we see that at the same flow rate the thickness of effective diffusion layer and the thickness of the boundary layer behave differently with changing temperature. Within the temperature range from 1 °C to 50 °C, increasing flow rate from 0 to 3.7 cm/s, the change of boundary layer thickness is around 1 mm and the change of diffusion layer thickness is about 10~20 μm . Even if the diffusion layer

thickness at 3.7 cm/s is reduced to half of the static polishing condition, the thickness of the diffusion layer is still far beyond the surface roughness (tens of nanometers). The surface roughness we measured did not show a correlation to the change of the diffusion layer thickness within this range. In order to achieve a more dramatic diffusion layer thickness change (for example, comparable to the surface roughness scale), the flow rate will need to be increased to more than hundreds of times faster. This may not be practical for cavity EP process.

Based on our analysis we may anticipate that for current cavity EP practice, the variation of the flow rate near the cavity inner surface at constant temperature will not cause non-uniform removal.

3.4. Conclusion

We studied the effect of surface flow rate on polishing rate and resultant topography during EP of niobium. The flow rate range we studied covered the flow rate in real cavity EP process. Current-time curve showed that the total current increased slightly as the surface flow rate increased from 0 to 3.7 cm/s during niobium flow-EP. However, the change in polishing rate within this flow range was not significant enough to affect the mass loss of niobium samples. The primary EP process was not changed by surface flow rate in this range.

The final surface topography and PSD from different flow rate also did not vary significantly. The RMS roughness on micro scale (50 μm x 50 μm) was slightly decreased with increasing flow rate, while the RMS roughness on macro scale (500 μm x 500 μm) was not affected by flow rate. The thickness of the effective diffusion layer on

niobium decreased with the surface flow rate during EP. This may contribute to the slight increase in total current and smaller height variation on micro scale.

Even though our study indicates that 0~3.7 cm/s surface acid flow at constant temperature has no significant influence on the removal rate and the large scale surface roughness, it still can be beneficial to have surface flow during cavity EP process, for possible improvements on micro scale surface roughness and more uniform temperature distribution in the electrolyte. No significant improvement in polishing rate can be made within operationally feasible ranges with current production setup.

CHAPTER 4

Laser Polishing of Niobium for SRF Applications – Parameter Optimization

4.1. Introduction

For mechanical or (electro-) chemical polishing, the effects are all achieved by attacking metal with aggressive media. None of the present options can be environmental friendly and time saving at the same time. To significantly improve a technology, some thinking out of the box is needed; the idea of laser polishing appears completely out of the box of the traditional methods. With no chemistry or foreign materials involved, the polishing may be done by re-arranging the atoms on the material surface. One merit of laser polishing is that polishing is done in a dry environment. This provides the possibility of a quick repair on the cavities in cryomodules that have been operated for a while and need to be refurbished. With promising results from our group [114], we are looking forward to prepare this technique for cavity/cryomodule application.

4.1.1. Motivation of laser polishing study

The final step in the production of niobium SRF accelerator cavities is removal of ~ 100 μm from the interior surface [90] by chemical and/or mechanical methods in order to remove contaminants and damage. Buffered chemical polishing (BCP), which provides a

niobium surface etch with a mixture of hydrofluoric, nitric acid and phosphoric acids has long been the dominant process because of simplicity and effectiveness. Electro-polishing (EP) with a hydrofluoric – sulfuric acid mixture sees increasing use as a final step to remove performance-limiting [29] [50] sharp features caused by BCP, but suffers a slower etching rate and uses a more complex setup [63]. Both involve hazardous acids and have potential for hydrogen contamination problems. Therefore, pursuit of greener and/or faster treatment methods has never stopped. Centrifugal barrel polishing (CBP), a mechanical method, avoids aggressive chemical and provides mirror-like surface, but the price is much longer polishing time. CBP may use a light EP as a final step [115] [116]. Other approaches being investigated include non-HF EP [108] [117] [118] [65] [64], plasma etching [119] [120] and laser polishing [114] [121].

4.1.2. Laser-material interaction fundamental and laser polishing concept

Laser processing is based on the interaction between laser light and matter. The mechanism of interaction depends on laser parameters and the physical and chemical properties of the material. Laser parameters include the wavelength, intensity, spatial and temporal coherence, polarization, angle of incidence and dwell time (illumination time at a particular site). Material properties include its chemical composition and microstructure. When an infrared (IR) laser interacts with metal, free electrons are excited. The excitation energy is dissipated into heat within a short time. Laser beam with low to medium intensities can be considered as a heat source inducing a temperature rise on the surface and into the bulk of the material. The temperature distribution is determined by the optical and thermal properties of the material. If there is phase

transition involved, the transformation energy for melting, boiling, crystallization, etc. will affect the temperature distribution.

A well-established application of laser processing is ablative laser machining, such as drilling, scribing, cutting, trimming, and shaping. In these cases, the material is removed from the work piece as liquid, vapor or plasma, with a laser intensity of about 10^5 to 10^{10} W/cm² and irradiation time from 10^{-7} to 10^{-1} s [122]. Lasers can also perform morphological, structural and compositional transformations on materials. Keeping the surface temperature just below or slightly above the melting temperature with proper laser intensity and pulse length, lasers can perform annealing, transformation hardening, glazing, recrystallization, alloying, and shock hardening. These applications require lower laser intensities, typically 10^3 - 10^8 W/cm².

Laser polishing relies on beam heating to partially melt the metal surface. Partial melting (or shallow surface melting, SSM) is preferred over formation of a full liquid surface layer (or surface overlayer melting, SOM) [123]. The absence of a fully-formed surface melt layer avoids hydrodynamical effects such as the formation of ripples that can remain upon solidification, a potentially harmful sharp roughness. Usually pulsed lasers are used so that the melt duration is short and cooling happens quickly. During the short melt period (a few nanoseconds), the surface tension works to smooth out sharp features. The final smoothening is the consequence of the total melt duration, the sum of all pulses delivered to a location. Since the effect of any pulse is reduced by the cumulative smoothening resulting from previous pulses, it is expected that there will be an optimum total melt time (i.e., number of laser pulses) for cost effectiveness.

Laser polishing has received researchers' attention for years, and significant experience has been gained. Examples include using CO₂ lasers and diode lasers to polish tool steel by removing surface patterns from machining [124]. Pulsed laser micropolishing (PLμP) as an alternative to chemical mechanical polishing (CMP) on nickel [125] not only reduced surface roughness but also increased corrosion resistance, as was also found on stainless steel after laser polishing [126]. Titanium medical implant material revealed a decrease of surface contamination and thickening of oxide layer after laser polishing [127]. Laser polishing is also applied to optical glass [128]. It was found that laser polishing reduced the RMS surface roughness of mechanically-polished only niobium from 700 nm down to 200 nm [114]. Within the fluence range of 0.6 ~ 2.3 J/cm² and 80 ~ 900 pulses overlapping, both SMM and SOM contributed to the resulting surface. This shows laser polishing of niobium SRF cavity is promising and that there is opportunity for further improvement as well.

4.1.3. Scope of this study

The present study aims at exploring in detail a wider range of polishing parameters, seeking even better surface finishing. The parameters to be optimized are fluence (energy per unit area per pulse) and pulse displacement. Pulse displacement is defined as the distance between the centers of two consecutive pulses. The product of pulse displacement and number of pulses overlapped equals one spot width. This is actually a measure of total energy deposition density onto the metal surface.

4.2. Simulation

Before undertaking experiments, it is desirable to obtain a sense of the range of key parameters and their effects. Previous study showed that a straightforward single pulse analysis provides insight [114]. It is not the purpose of such a model to accurately represent the complete process in detail, but rather to guide the experiments. In that regard, a useful benchmark is the energy requirement to bring niobium surface into the SSM melt range in a single pulse.

Here a simplified model was used to simulate laser polishing as described in [114].

A one-dimensional conduction heat transfer equation eqn. (1)

$$\frac{\partial T(z,t)}{\partial t} - \frac{\partial}{\partial t} \left(k(T) \frac{\partial T(z,t)}{\partial t} \right) = \frac{A(z,t)}{\rho(T)c_p(T)} \quad (1)$$

is used to model the temperature at the center of the laser spot, where $T(z,t)$ is the temperature at depth z at time t , ρ is the mass density, $k/\rho c_p$ is the thermal diffusivity, k' is the specific thermal conductivity, and c_p is the specific heat capacity. The material is treated as a one-dimensional semi-infinite solid, because the diameter of the melted zone is large compared to the melt depth ($\sim 100 \mu\text{m}$ vs. $\sim 100 \text{ nm}$ respectively). The source term,

$$A(z,t) = \alpha I(t)(1 - R)e^{-\alpha z} + \Delta U(z,t) \quad (2)$$

includes heat generated by absorption of the Gaussian laser pulse

$$I(t) = I_o e^{-(t-t_o)^2 / 2\sigma^2} \quad (3)$$

where α is the optical absorption coefficient, and R is the optical reflectivity at the laser wavelength. In Eqn. 2, $\Delta U(z,t)$ represents the internal heat sinks associated with the latent heat of the phase transformations of the material. Cooling is by conduction only; no radiant or convective heat loss was considered. The material is homogeneous and the

density, ρ , is taken to be constant, but temperature dependent values for k' and c_p are used in the finite difference method applied to numerically solving Eqn. 1. While this method provides an excellent tool for simulating the temperature profile produced by absorption of a laser pulse, the wide range of local surface topography may have an even larger impact on the actual temperature profile realized on real Nb samples.

A plot of the simulated surface temperature is shown in Figure 4.1. The dashed line corresponds to the melting temperature and the dotdash to boiling. The figure shows the time course of surface temperature associated a single 8 ns laser pulse for the indicated fluences, and the heat sink due to the latent heat of melting is apparent, particularly during cooling.

The simulation also computes the temperature vs. depth profile and the maximum depth of melting which can play an important role in the resulting laser polished surfaces. The maximum melt depth is 375 nm for a fluence of 2.75 J/cm^2 , 127 nm for 2.25 J/cm^2 , and 60 nm for 2.0 J/cm^2 . We note that these conditions readily allow for recrystallization of the superconducting RF penetration depth ($\sim 40 \text{ nm}$). Recrystallization may help improve the crystal quality in the surface layer from mechanical damage or impurities. This raises the prospect that rather than needing to remove the "surface damage layer" following fabrication by chemical or mechanical means, one may be able to directly "heal" the surface thus significantly simplify the niobium cavity preparation process.

The accumulation of residual heat when multiple laser pulses are incident on the surface has also been simulated, and the results indicate a small sequential rise in the peak temperature and melt depth for each laser pulse. On the other hand, at the fluence conditions for laser polishing, the reflectance of the real Nb surface will improve

sequentially with each laser pulse, resulting in falling absorption (heating) with each pulse. This effect counters the residual heat accumulation, helping to regulate the peak temperature and melt depth over the treatment of many laser pulses.

Figure 4.41. The simulated surface temperature for Nb due to the absorption of a 8 ns 1064 nm laser pulse for varying fluence values. The melting and boiling temperature are shown as dash and dot/dash lines respectively.

To summarize, the expected sequence of events is that a pulse arrives at an ambient temperature surface. The surface temperature rises until the end of the pulse, followed by temperatures below the surface. Accumulating heat from previous pulses to the same location will move the fluence requirement for melting temperature lower. Differences of surface topography arising from different prior processing history can affect

absorption of the laser beam energy, leading to differences in heating. Further, each successive pulse is expected to bring a corresponding increment of smoothening. This will change both the energy absorbed from the beam and reduce the extent of further smoothening during the melt duration from the present pulse. Uncertainties aside, this simple simulation serves to direct attention to the range of a few-tenths J/cm² per pulse, with details to be resolved by experiment.

4.3. Experimental Methods

4.3.1. Laser treatment system

A Spectra-Physics High Intensity Peak Power Oscillator (HIPPO) table top laser (Figure 4.2), optimized for micromachining, operating at 1064 nm was used as the laser source. The beam was measured to be a Gaussian with a Spiricon CCD camera based beam profiler. The beam was directed (Figure 4.3) into the UHV chamber of a PLD-5000 System (Figure 4.4) from PVD Products Inc. The nominal angle of incidence of the laser beam on sample was 60°. The focused spot size on the sample was 62 µm x 124 µm as measured by a knife-edge technique at the sample surface. The beam intensity at the sample position was measured as the change in reflected intensity when traversing a razor blade across a high reflectivity sample. The repetition rate was 19 kHz, and the pulse length at this repetition rate was about 8 ns. The sample holder was located at the center of the UHV chamber, as shown in Figure 4.5 and Figure 4.6, and each sample could rotate individually with a speed up to 60 rpm. During polishing, the sample rotating speed was adjusted accordingly to satisfy the pulse accumulation requirement. The chamber was pumped down to $\sim 10^{-7}$ - 10^{-8} Torr before the polishing experiments. The pressure during polishing never exceeded the high 10^{-7} Torr range.

Figure 4.42. Spectra-Physics High Intensity Peak Power Oscillator (HIPPO) table top laser used as the laser source in the laser polishing experiments

Figure 4.43. Optics to steer laser beam from laser source into the PLD-5000 System

Figure 4.44. PLD-5000 system from PVD Products Inc.

Figure 4.45. Vacuum chamber of the PLD-5000 System

Figure 4.46. The sample holder in the vacuum chamber of the laser treatment system. It can accommodate three samples at a time. The other three are for liquid target.

Reflectivity of niobium as a function of incident angle can be calculated with the equations below [9]:

$$R_p = \frac{[n - (1/\cos \phi)]^2 + \kappa^2}{[n + (1/\cos \phi)]^2 + \kappa^2}$$

$$R_s = \frac{(n - \cos \phi)^2 + \kappa^2}{(n + \cos \phi)^2 + \kappa^2}$$

The reflectivity as a function of incident angle is plotted in Figure 4.7. Our experiment setup delivered p-polarized incident light onto the sample with 60 degree incident angle, therefore the reflectivity is 66.69%.

Figure 4.47. Reflectivity of niobium for 1064 nm light at different incident angles

4.3.2. Material and preparation

The niobium samples were 49 mm diameter disks (Figure 4.8) cut from 3.2 mm thick sheet material of the type used for cavity fabrication. BCP practice varies in etch time and conditions depending on the application. We previously [75] [74] [86] reported

that even a few microns removal by BCP produces the same topography as heavy removal, as revealed by power spectral density (PSD) analysis of atomic force microscopy data (see later). To enable multiple etch/polish cycles with the same samples, we employed a light etch, one minute in 1:1:1 BCP solution at 23°C, rinsed with de-ionized water and air dried. This procedure is used at Jefferson Lab to prepare cavities for welding. The sample disks were then loaded into the laser treatment system and the chamber evacuated.

Figure 4.48. A niobium sample disk with laser treated rings

4.3.3. Polishing parameters

The fluence and the pulse accumulation were the two main parameters studied. The fluence was the energy density per pulse. The pulse accumulation could be expressed as the number of pulses overlapped within one spot width, or pulse displacement. During laser polishing the sample rotated about its own center at the chosen speed, while the beam was kept stationary or traversing along a radius. The target rotation was adjusted according to pulse accumulation required. With a stationary laser beam, each revolution of the target produced a polished single circle track on the sample. Changing the beam location on the sample yielded a series of concentric circles on the disks. Single track experiments were used for parameter optimization; Table 4.1 summarizes the range of these parameters explored. With laser beam moving along the radius of the sample in a series of steps, a ring comprised of multiple tracks could be produced. This experiment was used to explore the feasibility of treating large areas by beam rastering. The overlap fraction between tracks was explored from 0 to 100%, seeking the smallest overlap that gave no visible seam.

Table 4.7. Laser Irradiation Parameters

Laser power	Fluence	Number of pulses overlapped	Pulse displacement	Scan speed
W	J/cm ²	Within one beam width	μm	cm/s
1.51~10.98	0.68~4.96	10~670	6.2~0.14	11.78~0.27

4.3.4. Characterization

After laser treatment, the topography was examined by optical microscopy (HIROX KH-7700 High Resolution Digital-Video Microscopy System, Figure 4.9) and atomic force microscopy (AFM) (Digital Instruments Nanoscope IV, Figure 4.10). AFM was done in tapping mode with silicon tips and the scan size was $25\text{ }\mu\text{m} \times 25\text{ }\mu\text{m}$ or $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ for each image. Each AFM image consisted of 512 scan lines and there were 512 data points for each line. Root mean square (RMS) roughness values were obtained from these AFM data.

As discussed at length previously [86], roughness values are not a sufficiently incisive view of topography for the present purpose. The optics community encountered this issue long ago and turned to Fourier analysis to provide a direct view of the contributions at different length scales, power spectral density (PSD). PSD routines are found in the software packages accompanying AFM's, but they do not deal with a number of issues. It was therefore necessary to develop our own software, described elsewhere [75]. The understanding of detailed analysis of PSD data from SRF cavities is still advancing, but some inferences can reliably be made. As noted by optics researchers, sharp features lead to a straight line on a log/log plot. Rounding the sharp edges leads to relatively greater intensity loss at short wavelengths. The topography arising from certain processes (BCP, EP) gives rise to characteristic PSD plots, useful as fingerprints, while development of a more fundamental understanding proceeds. Power spectral density (PSD) analysis was applied to the AFM data using a program developed by one of our colleagues, C. Xu [75] (Figure 4.11). For all the surfaces, we used a second order de-trending and a Blackman window during the analysis.

Figure 4.49. HIROX KH-7700 High Resolution Digital-Video Microscopy System for optical inspection of samples

Figure 4.50. AFM (Digital Instruments Nanoscope IV) scan setup of laser treated niobium disk

Figure 4.51. PSD program interface for calculating PSD plot from AFM data

4.4. Results and discussion

4.4.1. Effect of fluence on topography

We studied the effect of varying fluence at fixed pulse accumulation. With the simulation result in mind, we covered a wider range of fluences (0.68~4.96 J/cm²) than the simulation to check our estimation. This also helps taking care of the offset between idealized model and realistic conditions.

Figure 4.12 shows the optical image of niobium surface after laser treatment at 4.96 J/cm² and 2.94 J/cm². The pulse accumulation was 53 pulses overlapped within one spot width.

Figure 4.52. Optical microscope image of niobium surface after laser treatment: (A) 4.96 J/cm², 53 pulses overlapped. (B) 2.94 J/cm², 53 pulses overlapped.

Since our interest was in the polishing region, we decided to lower the fluence range to 0.68 ~ 2.71 J/cm². At the same time, we reduced pulse accumulation to 34 pulses

overlapped within one spot width. Here we were looking for the lower limit of fluence having polishing effect on niobium surface. Figure 4.13 shows the optical image of niobium surface after laser treatment at 2.27, 1.13, 0.90, and 0.68 J/cm².

Figure 4.53. Optical images of niobium surface after laser treatments: (A) 2.27 J/cm^2 . (B) 1.13 J/cm^2 . (C) 0.90 J/cm^2 . (D) 0.68 J/cm^2 . Pulse accumulation was 34 pulses overlapped per spot width, equivalent to 1.8 μm pulse displacement or a scanning speed of 3.5 cm/s .

Figure 4.14 shows the AFM images of niobium surface received laser treatment at 0, 0.68 , 0.90 , and 1.13 J/cm^2 , with 34 pulses overlapped. Figure 4.14 (A) is a typical BCP

surface. The crater and the sharp edge are signatures of chemical etching. Figure 4.15 (B) is a slightly over melted surface, where the ripples pile up resulting a rough surface. Figure 4.15 (C) and (D) are both polished surfaces, where the sharp edges from BCP are smoothed but no new roughening is introduced.

(A)

(B)

(C)

(D)

Figure 4.54. AFM images of the niobium surface after laser treatment, with 34 pulses overlapped and fluence indicated. (A) BCP surface without laser treatment; (B) 1.13 J/cm^2 ; (C) 0.90 J/cm^2 ; (D) 0.68 J/cm^2 . Scan area 25 μm x 25 μm . Horizontal scale: 5 μm per division. Vertical scale: 0.5 μm per division.

Figure 4.15 presents the PSD analysis corresponding to the AFM images in Figure 4.14. The BCP treated surface shows the characteristic straight line on the log-log plot of PSD. The polished surfaces show a concave curve where the PSD values at high frequencies are lower than the BCP curve. 0.68 and 0.90 J/cm^2 laser treatment produced a

smoothened surface, while 1.13 J/cm^2 laser treatment produced a surface having critical topographic features similar to the starting BCP surface. We would attribute the 0.68 and 0.90 J/cm^2 case to SMM, while the 1.13 J/cm^2 case shows more evidence of SOM [124]. Similar changes for BCP surfaces subjected to EP have been reported [74] [75] [86].

Figure 4.55. PSD of niobium surface after laser treatment with different fluence, with 34 pulses overlapped. The four curves are calculated from the AFM images shown in Figure 4.14.

To summarize the effect of fluence on polishing effect, our experiments showed that above 1.13 J/cm^2 , with 34 pulses overlapped, the surface was over-melted. For 0.90 J/cm^2 and 0.68 J/cm^2 with the same pulse accumulation, there was no over-melting on the surface. Therefore, for 34 pulses overlapping, we suggest $0.68\sim 0.90 \text{ J/cm}^2$ to be the proper fluence range for polishing.

4.4.2. Effect of pulse accumulation on topography

We studied the effect of varying pulse accumulation at a fixed fluence at 2.27 J/cm^2 . The number of pulses overlapped (accumulated) within one pulse width (one beam spot diameter) ranged from 10 to 360. The surface was slightly over-melted around 34 pulses and the surface became damaged for pulse accumulations much greater than 34 pulses. 21 pulse accumulation was in the region where the surface is just melted to the desired degree to smooth out the sharp features without introducing over-melting features, what we defined as polished. For 10 pulses accumulation, the laser treatment track was difficult to find in the optical picture but did show polishing effect under AFM. Figure 4.16 shows selected optical images of surfaces after laser treatment at 2.27 J/cm^2 with 335, 50, 34, 21, and 10 pulses overlapped within one spot width.

Figure 4.56. Optical images of niobium surface after laser treatment at fluence of 2.27 J/cm^2 with different pulse accumulation. (A) 335 pulses. (B) 50 pulses. (C) 34 pulses. (D) 21 pulses. (E) 10 pulses. 21 pulses accumulation achieved the best smoothness. This is equivalent to $3.0 \text{ } \mu\text{m}$ pulse displacement or a scanning speed of 5.6 cm/s .

We narrowed our scan range down to 36~50 pulses overlapped with the fluence fixed at 2.27 J/cm^2 . This is like a “fine tuning” process looking for the transition number between polishing and damaging. Figure 4.17 shows the selected optical images of niobium surface after laser treatment at fluence of 2.27 J/cm^2 with 36~50 pulses overlapping. It turned out that we were not too far away from the upper limit of number of pulses overlapped needed in the polishing region. When 37 pulses overlapped, the surface already started to show evidence of overheating.

(A) r3

(B) r2

Figure 4.57. Optical images of niobium surface after laser treatment at 2.27 J/cm^2 with different pulse accumulation. (A) 38 pulses. (B) 37 pulses. (C) 36 pulses.

Figure 4.18 shows the AFM images of niobium surface after laser treatment at 2.27 J/cm^2 with varying pulse accumulation. The number of pulses overlapped (accumulated) within one pulse width (one beam spot diameter) shown here were 10, 21, and 34. Polishing effect is shown for 10 pulses accumulation here. 21 and 34 pulse accumulation showed polishing effect as seen in the optical images. Figure 4.19 is the corresponding PSD analysis of the images in Figure 4.18. From 11 to 23 and then 34 pulses overlapped, the PSD shows steady improvement of surface smoothness.

(A)

(B)

(C)

(D)

Figure 4.58. AFM image of niobium surface after laser treatment with constant fluence ($2.27 \text{ J}/\text{cm}^2$) and varying pulse accumulations. (A) untreated BCP surface. (B) 10 pulses. (C) 21 pulses. (D) 34 pulses. Scan area $25 \mu\text{m} \times 25 \mu\text{m}$. Horizontal scale: $5 \mu\text{m}$ per division. Vertical scale: $0.5 \mu\text{m}$ per division.

Figure 4.59. PSD of BCP treated niobium surface and the surface after laser treatment with a fluence of 2.27 J/cm^2 and different pulse accumulation (10, 21, and 34 pulses accumulated within one spot width). The four curves are calculated from the AFM images shown in Figure 4.18.

4.4.3. Effect of overlapping ratio in multi-track treatment on topography

In order to achieve laser treatment in a larger area, the laser beam was stepped along the radius while the target was rotating. The track of the laser beam spiraled from the edge towards the center of the disk, each circle overlapped with the next one at a chosen ratio. Using an optimized combination of fluence and pulse accumulation (1.13 J/cm^2 , 34 pulses accumulated within one spot width), we were able to treat larger area by overlapping tracks at different ratios. Figure 4.20 shows the optical image of niobium surface treated with overlapping ratio of 0.6, 0.7, and 0.983. Here the overlapping ratio is

The removal of sharp edges on the surface is apparent.

PSD calculated from the AFM images in Figure 4.21. The smoothing effect from different overlapping ratios is very similar.

Figure 4.60. Optical image of niobium surface after laser treatment at 1.13 J/cm^2 and 34-pulse accumulation. Each ring consists of five tracks overlapping with their neighbors. The overlapping ratios between two neighbor tracks tested varied from 0 to 100%. Above are selected images with overlapping ratio of: (A) 0.6 overlapping; (B) 0.7 overlapping; (C) 0.983 overlapping.

(A)

(B)

(C)

(D)

Figure 4.61. AFM image of niobium surface after laser treatment at $1.13 \text{ J}/\text{cm}^2$ and 34 pulse accumulation. Each laser treated ring consists of 5 laser tracks overlapping with each other at chosen ratio. (A) untreated BCP surface. (B) 0.6 overlapping. (C) 0.7 overlapping. (D) 0.983 overlapping.

Figure 4.62. PSD of niobium surface after laser treatment at 1.13 J/cm^2 and 34 pulse accumulation. The four curves are calculated from the AFM images shown in Figure 4.21.

4.4.4. Summary of polishing parameters

Figure 4.23 summarizes the parameter space we explored in this study. Figure 4.23 (A) shows all the parameters tested. The triangles represent conditions where no polishing was found or over-melting happened, and the circles represent conditions where polishing was achieved. Figure 4.23 (B) shows an enlarged plot of the polishing region only.

We noticed that pulse accumulation and fluence are coupled when establishing the effective region. There is an upper limit of fluence at which one pulse could destroy the surface. There is also a lower limit of fluence where the surface will not be polished regardless of pulse accumulation. Between these two limits, polishing could happen as

long as the pulse accumulation is adjusted according to the fluence of each pulse. That means proper combination of fluence and scanning speed is important to achieve polishing effect. It also means there is some flexibility for choosing polishing parameters, even if not much. Given certain fluence, there is a narrow range for pulse accumulation that can provide partial melted surface; and vice versa. Since the pulse accumulation is related to scanning speed, this means one benefit of higher fluence is possibly a higher polishing rate, because fewer pulses are needed in a given area if the energy per pulse is high. This correlation between pulse accumulation and fluence is presumably related to the heat history left on the target by each pulse.

(A)

(B)

Figure 4.63. Summary of the parameters covered in this study. Triangle points are conditions where no polishing or over-melting happened. Round points are conditions where polishing happened. (B) is the polishing points magnified from (A).

For future research, it would be useful to continue this study with more precise control of the parameters and a wider range of variables accessible; for example, changing the pulse width, lower the repetition rate and changing the sample temperature. It would also be very helpful if the sample temperature and the topography could be closely monitored and perhaps controlled during the polishing process.

4.5. Comparing laser polishing with other polishing methods

We compared the topography of laser polishing (Figure 4.15, Figure 4.19) with that of the other surface treatment methods (Figure 4.24, Figure 4.25). Sample A was subjected to 100 μm removal by 1:1:2 BCP (“heavy BCP”). Sample B “EP” was first subjected to 100 μm removal by 1:1:2 BCP and then a further 50 μm removal by

electropolish, a heavy EP as previously described [129]. Sample C “CBP” is a typical CBP surface, prepared as described in reference [130]. The visible effect of EP on the PSD, even for as little as 5 μm removal [75] is to eliminate the straight line (power law) profile associated with the sharp edges of BCP, much as does laser polishing.

As shown in Figure 4.24, the EP surface is smooth everywhere without any sharp features. The wavy topography is probably due to the heavy BCP starting surface. The BCP surface is full of sharp edges due to etching. And the CBP surface has the smallest height variation but shows some special patterns on small scale. The different characteristics of these surfaces result from their very different polishing mechanisms. The laser polished surface most closely resembles the EP surface.

Figure 4.64. AFM images of niobium surface after: A) BCP; B) EP; C) centrifugal barrel polishing (CBP), Scan size was 50 μm x 50 μm . Horizontal scale: 10 μm per division. Vertical scale: 10 μm per division (A and C) and 5 μm per division (B).

Figure 4.25 presents the PSD analysis of the surfaces in Figure 4.24 in one plot for comparison. The BCP surface (square marker) shows almost a straight line going down at a slope of about 45° from $6 \times 10^{-5} \text{ nm}^{-1}$ to $5 \times 10^{-3} \text{ nm}^{-1}$. The EP surface (circle marker) shows a recession in the middle of the BCP downward 45° line from $6 \times 10^{-5} \text{ nm}^{-1}$ to $3 \times 10^{-3} \text{ nm}^{-1}$. We interpret this as the features in this frequency range were significantly reduced on EP surface comparing to BCP surface, with a turning point around $5 \times 10^{-4} \text{ nm}^{-1}$ where

the reduction slowed down and started to plateau out towards higher frequency. The CBP surface (star marker) curve shows lower PSD than the other curves over most of the frequency range except the slight hump around 10^{-3} nm^{-1} . Laser polished (LP) surfaces (Figure 4.15, Figure 4.19) show concave curvature having a lower PSD value than BCP line being from $4 \times 10^{-4} \text{ nm}^{-1}$ to 10^{-2} nm^{-1} . We interpret this as the high frequency features (sharp edges) on BCP surface were reduced, while the lower frequency features of the background BCP surface stayed unchanged. The LP curve overlapped the EP curve towards the high frequency end and at the low frequency limit, meaning the features within this range were similar on these two types of surfaces.

Figure 4.65. PSD analyses of the BCP, EP, and CBP surfaces corresponding to the AFM images in Figure 4.24.

4.6. Conclusion

Laser polishing of niobium was achieved by controlling fluence and pulse accumulation. Images and PSD analysis showed that the best polishing result was below a fluence of 0.90 J/cm^2 . At this fluence range, 34 pulses overlapped within one spot width provided the smoothest surface. The fluence could vary from 0.57 to 0.90 J/cm^2 if adjusting the pulse accumulation accordingly.

Larger area polishing was achieved by rastering laser tracks next to each other with appropriate overlapping ratio. At optimized fluence and pulse accumulation, laser tracks overlapping at a few ratios all showed smoothed surface.

Comparison of topography and PSD analysis of laser polishing with other polishing methods shows that laser polishing smooths sharp features of niobium in a way similar to EP. Having established that a laser can produce smooth surfaces encourages us to proceed towards the application of laser polishing to extended niobium surfaces.

CHAPTER 5

Laser Polishing of Niobium for SRF Applications – Application on different surfaces

5.1. Introduction

The topography that impacts the performance of SRF cavities arises during the manufacturing process. Details differ somewhat among the organizations, but the main steps at the Jefferson Lab (JLab) SRF Institute have much in common with those elsewhere. The standard niobium starting material is specially purified and processed sheet, about 3 mm thick with a $\sim 50\text{ }\mu\text{m}$ grain size. Discs are cut, deep-drawn and trimmed to form cups (half-cells). If needed to remove major defects, the cavities are mechanically polished. They are etched to remove a few μm of surface (“light BCP”) and e-beam welded to form the cavity. More than $100\text{ }\mu\text{m}$ is etched from the interior surface (“heavy BCP”) and the cavity is subjected to high pressure rinsing. BCP (buffered chemical polishing) is immersion in a 1:1:1 or 1:1:2 mixture of concentrated hydrofluoric, sulfuric and phosphoric acids [29]. For many years, cavities in this state were tested and assembled into cryomodules for installation in the accelerator. Such would be the surface condition of cavities coming from cryomodules being routinely cycled out for maintenance. Currently new production cavities are electropolished

(“EP”) to remove a further 30 μm from the interior surface before the final low temperature bake. Alternative schemes are being investigated, including polishing-chemistry free of hydrofluoric acid and more extensive mechanical polishing. For example, at JLab centrifugal barrel polishing (“CBP”) is being tested as a substitute for the BCP heavy etch, leaving only the 30 μm removal by EP [115] [131] [116] [132].

All these approaches combine mechanical and chemical polishing of various sorts in varying degrees. They may bring improvements, but they are not likely to be game-changers. Moreover, the increasing standards for gradient and energy efficiency are forcing cavity builders toward 100% inspection of the interior surface. As an alternative, laser polishing offers some attractive benefits. Among the most advantageous: no chemistry, no surface contact, simultaneous monitoring and option to re-do all or part of the surface. To fully realize these benefits, a lengthy journey lies ahead to the point where the accelerator community can utilize laser processed accelerating cavities in an operating machine. The small step presented below aims to demonstrate that laser polishing can attain the topography and chemistry needed, given the expected range of starting surface conditions.

Laser polishing relies on optical beam heating to partially melt the metal surface. Partial melting of the surface (or shallow surface melting, SSM) is preferred instead of formation of a full liquid surface layer (or surface over-melting, SOM) [123]. Usually pulsed lasers are used so that the melt duration is short and cooling happens quickly. During the short period of melting (a few nanoseconds), the surface tension works to smooth out sharp features. Recall that sharp surface features are harmful to cavity performance. The absence of a fully-formed surface melt layer avoids hydrodynamic

effects such as the formation of ripples that can remain upon solidification, resulting in a harmful sharp roughness. The final smoothening is the consequence of the total melt duration, the sum of the effect of all pulses delivered to a location. Since the effect of any single pulse is reduced by the smoothening from previous pulses, it is expected that there will be an optimum total melt time (= number of laser pulses) for best process efficiency.

Laser polishing could be inserted at a number of points in the process for new cavities, beginning with the completion of mechanical assembly. It could also be applied to existing cavities as the cryomodules in which they are housed are routinely cycled out for refurbishment. Several surface conditions need to be examined as starting points: mechanically polished only, centrifugal barrel polished (CBP), light BCP and heavy BCP (existing cavities). A surface condition with essentially no initial topography is provided by coupons that have been metallographically polished to $< 50 \text{ nm } R_a$, termed nano-polished (“NP”) in our previous work. Such smoothness facilitates application of the characterization techniques discussed later.

In this study, we selected a few different starting surfaces for laser polishing, including CBP surface, mechanical polished surface, and weld preparation surface. These are all surface conditions expected for cavity production. Laser polishing was done on these surfaces using the optimized parameters in the previous study. Knowing the effect of laser polishing on these surfaces helps us learn how laser polishing can be integrated into cavity fabrication. We also compared the topography of laser polished niobium surface with surfaces produced from other polishing methods.

5.2. Experiment

5.2.1. Material and preparation

Niobium squares 1 cm x 1 cm were cut from 3 mm-thick sheet material used for cavity fabrication.

For the “CBP” surface, a niobium tube was internally polished in the CBP equipment, operating as described in reference [132], and then squares were cut from the tube by electrical discharge machining (EDM).

For the mechanical polished surface, the niobium squares were polished to mirror finish with silicon colloidal of 0.1 μm diameter.

For the welding preparation surface, the niobium squares were lapped (mechanical polishing with rough sanding material) and treated 1:1:1 BCP at ambient temperature for 1 minute (“light BCP”). A further sample set was subjected to 1:1:2 BCP for time sufficient to remove mass equivalent to 120 μm (“heavy BCP”).

Finally, nanopolished samples (“NP”) (see later) were prepared for SIMS. The quotes above indicate the name by which each item is called later. All samples were cleaned ultrasonically with detergent and de-ionized water after polishing. They were then dried and loaded onto the sample holders in the laser treatment apparatus.

5.2.2. Laser treatment

A Spectra Physics High Intensity Peak Power Oscillator (HIPPO) micromachining laser operating at 1064 nm provided the source for laser polishing. The repetition rate was 19 kHz, and the pulse length was about 8 ns. The beam was directed into the process chamber of a PLD 5000 system from PVD Products Inc. The angle between the incident beam and the metal surface normal was 60°. The beam incident onto the niobium surface

was p-polarized, with a nominal reflectivity of ~68%. The sample holder could accommodate three discs and each disk could rotate at a speed up to 60 rpm. The square samples were fit into three aluminum discs, each having four 1 cm x 1 cm openings to hold up to four square sample coupons. The focused spot size on the sample was 62 μm x 124 μm FWHM (2σ of Gaussian beam, equivalent to a spot area of $6.04 \times 10^{-5} \text{ cm}^2$). The spot size was measured separately by monitoring the intensity of the beam reflected from a highly polished sample as a razor blade traversed the beam spot on the sample surface. The vacuum chamber was pumped down to 10^{-7} ~ 10^{-8} Torr before the polishing and never exceeded 10^{-7} Torr during each run.

Polishing parameters were chosen according to previous studies [133]. The fluence studied was from 0.67 J/cm² to 1.12 J/cm², with 34 pulses accumulated in one spot width.

5.2.3. Characterization

The samples were examined with optical microscopy (HIROX KH-7700 High Resolution Digital-Video Microscopy System) and scanning electron microscope (SEM - Phenom G2 Pro desktop SEM, Figure 5.1). Atomic force microscopy (AFM - Digital Instruments Nanoscope IV) was applied to selected smooth-appearing areas to determine if indeed they were smooth as it is relevant for SRF – free of sharp features. AFM data were collected with "tapping" mode with a scan rate of 0.5 Hz. The scanned area was 25 μm x 25 μm , each scan comprising 512 equally-spaced points. Power spectral densities (PSD) were calculated from AFM data, as described in references [74] [75] [86].

Melt processing of the surface brings attention to the possibilities of grain re-growth vs the nucleation of new grains or perhaps other unanticipated outcomes. Electron back-scatter diffraction (EBSD) was used to visualize surface grain crystallographic

orientation. The work was carried out at the Nanoscale Characterization and Fabrication Laboratory at Virginia Tech, using a FEI Helios 600 Nanolab dual-beam FIB equipped with a Pegasus XM-4 EBSD system. The e-beam used was 2.7 nA at 20 kV with a 15 mm working distance.

It is also important to understand the chemistry of the surface layer due to the shallow RF penetration in the superconducting state (~40 nm) lends great importance to the chemistry of this layer. It is reasonable to inquire as to what effect laser polishing might have. We have previously employed secondary ion mass spectrometry (SIMS) to determine composition as a function of depth below the surface (sputter profile) of niobium materials [83]. The present measurements were performed by the Analytical Instrumentation Facility at North Carolina State University.

TOF-SIMS [134] is a highly sensitive surface analytical technique for acquisition of elemental and molecular information from the surface of a material with high spatial and mass resolution. A finely focused, pulsed primary ion beam is rastered across the surface of the sample and the secondary ions emitted at each irradiated point or pixel are extracted into a time of flight mass spectrometer, mass filtered, and counted. With dual beam operation, meaning sputtering with Cs ion beam and analyzing with liquid metal Bi ion beam, a depth profile of ions can be obtained. TOF-SIMS analyses were conducted using a TOF-SIMS V (ION TOF, Inc. Chestnut Ridge, NY) instrument equipped with a Bi_n^{m+} ($n = 1 - 5$, $m = 1, 2$) liquid metal ion gun and Cs sputtering gun. The analysis chamber pressure was maintained below 5.0×10^{-9} mbar to avoid contamination of the surfaces to be analyzed. For the depth profiles acquired in this study, 1 keV low energy Cs^+ with 10 nA current was used to create a $150 \mu\text{m} \times 150 \mu\text{m}$ crater, and the middle 10

$\mu\text{m} \times 10 \mu\text{m}$ area was analyzed using 25 keV Bi_3^+ primary ion beam at 0.35 pA current. The negative secondary ion mass spectra obtained were calibrated using H^- , C^- , O^- , AlO^- , Nb^- .

Figure 5.66. Phenom G2 Pro desktop SEM

5.3. Results and discussion

5.3.1. Effect of laser polishing on CBP surface

5.3.1.1. Topography and surface roughness

Figure 5.2 shows the optical and SEM image of laser polished CBP surface; the laser track is evident. The visual appearance of the CBP surface is mirror-like, but the microscopy reveals scratches and pits, even if the RMS value is only tens of nanometers. Figure 5.3 shows the AFM images of CBP surface before and after laser polishing. Small waviness was introduced by the laser polishing but the scratches and pits due to the CBP process were eliminated. The pre-and post-treatment roughness values (R_q) were 36 nm and 85 nm, respectively. These values are presented for comparison; they provide little insight into topography as it is relevant to SRF applications. The PSD analysis in Figure 5.4 presents another view of the topography change. After laser polishing, contribution from the lower frequency region (below $3 \times 10^{-4} \text{ nm}^{-1}$) increased, while contribution from the higher frequency region (above $3 \times 10^{-4} \text{ nm}^{-1}$) decreased. This accounts for the higher roughness value after treatment. The relatively gentle waviness is understood to be without adverse impact on SRF performance, in contrast with the small, sharp features that can reduce SRF performance. We note that application of PSD analysis to CBP topography studies appears not to have occurred within the SRF community previously. Further study is needed to gain deeper understanding.

(A)

(B)

Figure 5.67. (A) Optical and (B) SEM image of CBP niobium surface with laser polished track. Laser fluence was 0.71 J/cm^2 and pulse accumulation was 34 pulses per spot width.

(A)

(B)

Figure 5.68. AFM image of CBP niobium surface (A) before and (B) after laser polishing. Scan area $25\text{ }\mu\text{m} \times 25\text{ }\mu\text{m}$. Laser polishing fluence was $0.71\text{ J}/\text{cm}^2$ and pulse accumulation was 34 pulses per spot width.

Figure 5.69. PSD plot of CBP surface before and after laser polishing, calculated from the AFM data in Figure 5.3.

5.3.1.2 TOF SIMS analysis

In order to understand how laser polishing changes surface chemistry of niobium, depth profiles were obtained by TOF SIMS on the CBP niobium surface from previous session. Figure 5.5 shows the depth profile of hydrogen and oxygen related species on niobium surface before and after laser polishing. Figure 5.6 shows the depth profile of other species such as F-, C-, Si-, S-, Cl-, AlO-, PO2- (mostly from CBP polishing media) on niobium surface before and after laser polishing. Consider the green (NbH) and red (H) traces from the untreated sample in the major components spectra in Figure 5.5 (A). Both show a depressed value for the first 20-25 seconds of sputtering, corresponding to the surface oxide layer. It was found earlier that niobium oxide and niobium metal sputter at similar rates under the present conditions. Previous study [76] reported the

oxide layer thickness as 4-6 nm, depending on details, implying that the total sputter depth is of order 20-30 nm, well within the RF penetration depth. The only evident impact of laser polishing is that the oxide layer becomes slightly thinner. No evidence of contamination is apparent in the SIMS data.

Figure 5.70. SIMS sputtering profiles of major components of laser treated CBP niobium.

(A) Without laser polishing; (B) 0.67 J/cm^2 ; (C) 1.12 J/cm^2

Figure 5.71. SIMS depth profiles of other elements found on laser treated CBP niobium.

(A) Without laser polishing; (B) 0.67 J/cm^2 ; (C) 1.12 J/cm^2

5.3.2. Effect of laser polishing on mechanical polished surface

Figure 5.7 shows the optical and SEM image of mechanical polished surface with the laser polished area at the center. Figure 5.8 shows the AFM image of the mechanical polished surface before and after laser polishing. Figure 5.9 shows the PSD analysis of the surfaces corresponding to the ones in Figure 5.8. The mechanical polished surface was mirror-like and looked similar to the CBP surface visually, showing a small RMS roughness of 36 nm as CBP surface. Under SEM small scratches were observed, corresponding to a bigger contribution from high frequency in the PSD analysis. Laser polishing was able to remove these high frequency components, proved by both the PSD (the region above $7 \times 10^{-4} \text{ nm}^{-1}$) and microscopies. Notice that the PSD showed a linear

trend that is usually typical for BCP surface. This could be attributed to the pits and cracks after laser treatment due to non-uniform thermal properties of some contamination and possible over-melting at certain spots.

(B)

Figure 5.72. (A) Optical and (B) SEM image of mechanical polished niobium surface with laser polished track. Laser fluence was 0.71 J/cm^2 and pulse accumulation was 34 pulses per spot width.

(A)

(B)

Figure 5.73. AFM image of mechanical polished niobium surface (A) before and (B) after laser polishing. Scan area 25 μm x 25 μm . Laser fluence was 0.71 J/cm² and pulse accumulation was 34 pulses per spot width.

Figure 5.74. PSD plot of mechanical polished niobium surface before and after laser polishing, calculated from the AFM data in Figure 5.8.

5.3.3. Effect of laser polishing on light BCP surface

5.3.3.1. Topography and surface roughness

Figure 5.10 shows the optical and SEM image of light BCP surface with the laser polished region at the center. Before BCP, lapping as a coarse mechanical polishing was used to make the surface flat. Light BCP is a common step following lapping to clean the surface. Even for a short duration of 1 minute, the surface showed typical BCP etching pattern – accumulation of craters whose shape depends on the crystal orientation. Their edges are usually sharp. After laser polishing the craters and the sharp edges are smoothed. Figure 5.11 shows the AFM images of the surface before and after laser polishing at an area of 25 μm x 25 μm . The RMS roughness was reduced significantly from 321 nm to 175 nm after laser polishing. The PSD analysis in Figure 5.12 showed

that the roughness was reduced on all frequency ranges. Laser polishing shows more improvement when the starting surface is rough, such as BCP surface.

(B)

Figure 5.75. (A) Optical and (B) SEM image of light BCP niobium surface with laser polished track. Laser fluence was 0.71 J/cm^2 and pulse accumulation was 34 pulses per spot width.

(A)

(B)

Figure 5.76. AFM image of light BCP niobium surface (A) before and (B) after laser polishing. Scan area 25 μm x 25 μm . Laser fluence was 0.71 J/cm² and pulse accumulation was 34 pulses per spot width.

Figure 5.77. PSD plot of light BCP niobium surface before and after laser polishing, calculated from the AFM data in Figure 5.11.

5.3.3.2. EBSD

In order to understand how laser polishing changes the crystal structure of niobium surface, EBSD was conducted on light BCP niobium surface. Figure 5.13 shows an SEM image and the orientation map of the selected area analyzed by EBSD. The SEM image was from the previous light BCP sample, acquired at 70° tilt in the EBSD instrument. The area viewed by the EBSD camera (green outline) is foreshortened accordingly. The laser track extended from bottom left to upper right. No significant change of crystal orientation was found after laser polishing. The orientation of the surface grains followed the orientation of the substrate niobium with very little perturbation after laser treatment.

(A)

Figure 5.78. Orientation image map of the light BCP niobium surface with laser polishing tracks across the surface from EBSD analysis. (A) Corresponding SEM image containing orientation map area; (B) Orientation map of the boxed area in the SEM image. Area was $400\text{ }\mu\text{m} \times 400\text{ }\mu\text{m}$. Data acquired at $1.75\text{ }\mu\text{m}$ step size.

5.3.4. Effect of laser polishing on heavy BCP surface

Figure 5.14 shows the optical and SEM image of heavy BCP surface with the laser polished region across the center. Bulk BCP of more than 100 μm surface removal is usually used after machining and electron beam welding of an SRF cavity. Defects and contaminations introduced during the machining are removed by heavy BCP. The resulting surface is very shiny visually, but shows facets and ridges under microscopies. The height variation of the surface can be quite large at some locations. Usually an EP of tens of microns is applied to smooth these sharp features. Here we are looking at the effect of laser polishing on these sharp features. As shown in Figure 5.14, the sharp edges are rounded by the laser polishing. We noticed some fringes in the laser treated area, possibly caused by optical interference. Figure 5.15 shows the AFM images of the surface before and after laser polishing. Scan area was 25 μm x 25 μm . The PSD analysis in Figure 5.16 showed that the characteristic BCP straight line is significant reduced around the frequency of 10^{-3} nm^{-3} after laser polishing.

(A)

(B)

Figure 5.79. (A) Optical and (B) SEM image of heavy BCP niobium surface with laser polished track. Laser fluence was 0.89 J/cm^2 and pulse accumulation was 34 pulses per spot width.

(A)

(B)

Figure 5.80. AFM image of heavy BCP niobium surface (A) before and (B) after laser polishing. Scan area 25 μm x 25 μm. Laser fluence was 0.89 J/cm² and pulse accumulation was 34 pulses per spot width.

Figure 5.81. PSD plot of heavy BCP niobium surface before and after laser polishing, calculated from the AFM data in Figure 5.15.

5.3.5. Effect of laser polishing on nano-polished surface

5.3.5.1. Topography and surface roughness

Figure 5.17 shows the optical and SEM images of nano-polished niobium surface with laser treated regions across the center. The nano-polished surface is usually prepared by chemical-mechanical polishing to mirror finish and used for metallography study. The RMS roughness is on the scale of a few nanometers. Grain boundaries are barely evident under optical microscopy and SEM. Laser polishing introduced some wavy features. But the change in topography is not significant and the flat surface was conserved. No evidence of ablation was found by surface profile scan across the laser track. Figure 5.18 shows the AFM images of the surface before and after laser polishing. Scan area was 25

$\mu\text{m} \times 25 \mu\text{m}$. The PSD analysis in Figure 5.19 showed increased intensity at long wavelengths, in agreement with the waviness seen in the images.

(B)

Figure 5.82. (A) Optical and (B) SEM image of nano-polished niobium surface with laser polished track. Laser fluence was 1.0 J/cm^2 and pulse accumulation was 34 pulses per spot width.

(A)

(B)

Figure 5.83. AFM image of nano-polished niobium surface (A) before and (B) after laser polishing. Scan area 25 μm x 25 μm . Laser fluence was 1.0 J/cm² and pulse accumulation was 34 pulses per spot width.

Figure 5.84. PSD plot of nano-polished niobium surface before and after laser polishing, calculated from the AFM data in Figure 5.18.

5.3.5.2. TOF SIMS analysis

Figure 5.20 shows the depth profile of hydrogen and oxygen related species on nano-polished niobium surface before and after laser polishing. Figure 5.21 shows the depth profile of other species such as F^- , C^- , Si^- , S^- , Cl^- , AlO^- , PO_2^- (mostly from nano polishing media) on nano-polished niobium surface before and after laser polishing. The SIMS results from the other nano-polished samples were closely similar. Similar as we found on the CBP samples, the only evident impact of laser polishing is that the oxide layer becomes slightly thinner, the more so as fluence increases. No contamination was introduced by laser polishing. Non-relevant elements were slightly reduced by laser polishing.

(A)

(B)

(C)

(D)

(E)

Figure 5.85. SIMS sputtering profiles of major components of laser treated nano-polished niobium. (A) Without laser polishing; (B) 0.67 J/cm^2 ; (C) 0.89 J/cm^2 ; (D) 1.00 J/cm^2 ; (E) 1.04 J/cm^2 ; (F) 1.12 J/cm^2

(B)

(C)

(D)

(E)

Figure 5.86. SIMS depth profiles of other elements found on laser treated nano-polished niobium. (A) Without laser polishing; (B) 0.67 J/cm^2 ; (C) 0.89 J/cm^2 ; (D) 1.00 J/cm^2 ; (E) 1.04 J/cm^2 ; (F) 1.12 J/cm^2

5.4. Conclusion

Laser polishing with optimized parameters was performed on niobium surfaces that have been prepared by several different methods that are currently used or under development for SRF cavity production. They were examined by multiple characterization techniques. Especially in materials prepared by BCP, there was strong evidence of sharp edges, known to be associated with reduced SRF performance. Laser polishing rounded these and other sharp features significantly in all instances. Grain melt and re-growth offers the best description of the chief effect of laser polishing on surface

grain structure. Careful examination of the RF-active surface layer revealed no evidence of contamination as a result of the laser polishing process.

The fact that laser polishing not only eliminates surface sharp features but also improves surface grain structure by recrystallization makes it a promising replacement for surface polishing with chemistry.

CHAPTER 6

Summary

Steadily improving performance-for-cost is needed for solid niobium SRF accelerator technology. As discussed in Chapter 1, SRF cavity interior surface topography is a key point of impact. Recent work in our group has moved us forward from the day of “smoother is better” to a detailed description of what “smoother” is, how it may be measured and what impact it has. This progress motivated the present study. The aim is to advance fundamental understanding of the genesis of topography by the present and emerging surface treatment technologies so as to delineate what is attainable presently and, by a determined R&D effort, in the future. As discussed in more detail below, the major findings are:

1. BCP inherently and unavoidably leads to micron-scale roughness for conventional niobium sheet. Acceptable Q_0 values will require operation at surface fields corresponding to gradients below the upper teens of MeV/m. Alternative chemistries offered no indication of improvement.

2. EP yields suitable topography, but at a polishing rate about one-tenth the rate of BCP and with much greater process complexity. Varying the surface flow rate within a range compatible with present technology yielded no improvement in rate, but no loss of polishing effectiveness either. Going forward, each case will require judgment about whether the particular cavity geometry can accommodate the process requirements and

whether the value of the improved performance justifies the added cost. Nothing seen so far in the performance of alternative electrolytes points to a different conclusion.

3. Laser Polishing by partial surface melting was able to produce topography substantially equivalent to that obtained by electropolishing. However, the LP surface is the result of rapid thermal processing and may be expected to potentially house a population of defects considerably different from that of the well-annealed materials used in BCP and EP. What consequences, if any, may result is unknown.

6.1. Accomplishments

Surface polishing of niobium is an important step in the fabrication of SRF cavities. We carried out a series of experiments searching for ways to improve polishing techniques. Improvement in polishing techniques can be made in several aspects, including surface finish (topography), polishing rate, environmental concern, convenience for operation, cost of process, etc. We adopted the newly developed power spectral density (PSD) analysis as one of the characterization tools to evaluate the improvement on topography.

We investigated the possibility of improvement in buffered chemical polishing (BCP) and electro-polishing (EP) by varying polishing conditions. Besides further our understanding of polishing mechanisms, our studies also suggest ways to improve the surface finish and the polishing rate for these two methods.

For potential improvement in the longer run, we explored laser polishing as an alternative to chemical polishing methods. Laser polishing has obvious advantages in environmental concern because it is chemical free. Our experiments showed promising results in the surface finish from laser polishing. With investment in engineering setup, it

has potential advantages in convenience of operation/repair and cost of process for long term.

6.1.1. BCP

Advanced understanding of the generation of the BCP surface was gained. We found that the topography strongly depend on the grain size and orientation of the crystals. Evidence of different removal rates on different orientations was found. For single crystal, the height variation was not as large even after heavy BCP. Bi-crystal with two similar orientations showed no evidence of differential etching either. Therefore, the difference of removal rate is the main contributor to fine grain niobium BCP topography.

Gas evolution may contribute to some degree as well, since nitrogen oxides are produced on the surface of niobium during polishing. When the surface to be polished faced downward, the chance of getting bubble prints on the surface is higher. By creating relative motion between the metal and solution (stirring the solution or rotating the metal), the chance of getting bubble prints on the surface is greatly reduced.

For fine grain niobium, the resulting BCP topography depends on total removal. The removal rate is mainly decided by temperature and surface flow. From 0 to 20 °C, the removal rate increases with temperature and surface flow rate. The removal rate is less predictable at higher temperature as more factors will come into play and complicate the reaction.

Our study indicates that polishing rate can be improved with BCP by using proper temperature and surface flow. However, the topography is inherent with BCP and no improvement can be made by changing polishing conditions. Suggestions for cavity BCP practice, lower temperature and sufficient surface flow should be used, because a slower

etching provides a better control of total removal and the surface flow helps avoiding gas accumulation on the surface.

6.1.2. EP

EP is well known for its smooth surface finish and is already providing record-gradient for SRF cavities, despite the much lower polishing rate than BCP. We put our effort in improving the polishing rate of EP. We found that surface flow has some benefits for both polishing rate and surface roughness. In the range we studied, the polishing rate increases slightly with surface flow rate, indicated by the total current even if we did not detect significant mass loss difference. Improvement is also seen on micro scale roughness with increasing surface flow rate. Even if the improvement is not significant, we suggest the cavity EP practice adopt sufficient surface flow to obtain this benefit.

6.1.3. Laser polishing

We made a major step forward by showing that laser polishing is a promising alternative for surface polishing. We proved that laser polishing is capable of removing sharp features on the surface of niobium. The optimized laser fluence was from 0.57 to 0.90 J/cm². The pulse accumulation should be around 34 pulses per spot width and need to be adjusted accordingly to the fluence, e. g., higher fluence needs less pulse accumulation. The polishing effect was obvious with microscopy and confirmed by PSD. We polished larger areas by overlapping single laser tracks. With a more precisely controlled stage, polishing areas with specific shapes is feasible.

The polishing mechanism can be described with the shallow surface melting theory, proved by both simulation and experiments. Only tens of nanometers of the top surface layer were melted according to our simulation. No evidence of ablation was observed experimentally from cross section profiles. Some evaporation is possible since the surface is partially melted. The smoothing effect is more prominent with a starting surface with many sharp features. Laser polishing does not change the grain structure on a BCP treated surface. Reduction of contamination and slightly thinner oxide layer was observed after laser polishing. We do not see the potential of harming cavity performance from these findings. Proof from RF surface resistance measurement is needed though.

Using laser polishing, we successfully improved niobium surface topography produced by several different methods used in cavity fabrication, showing that laser polishing can be placed at different stages in the fabrication process. In addition to beneficial topography improvement, we also expect a quite acceptable polishing time from laser polishing. With our current setup, a few to tens of hours would be needed to cover the inner surface of a typical cavity. With a larger beam size, faster polishing could be achieved.

6.2. Future work

The work on laying down multiple adjacent tracks to cover an area needs to be refined and extended, but it is clearly within reach to eliminate sharp topography by this means. The most important question is then: does it help? Until recently answering this question required making a high quality coating on the interior of a single cell cavity, a major undertaking. Indeed a similar accomplishment is needed for most surface treatments, such as thin film deposition. Certainly some risk reduction is to be desired. To

this end, a surface impedance characterization (SIC) instrument has been developed. Briefly, it provides that a material of interest in the form of a 50 mm flat disc serves as one end of an RF cavity that can be cooled to below 2 K. Energy deposition with the experimental material is compared to a disc of reference material [135].

Success with flat discs will motivate scale-up to cavities. It is needed to accurately deliver a suitable sequence of laser pulses to every location on the interior surface of a cavity. Fortunately, future inspection requirements create much of the same need. It has been determined that it is needed to view every location as an image and to collect white light interferometry data to describe the topography. Further, it is needed to be able to deliver a laser beam able to repair damage spots that might be found. The machine (“CYCLOPS”) is in place and is undergoing commissioning [49]. It is not a far step to use it for the treatment purpose.

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