

# STUDIES OF ELECTROPOLISHING AND OXYPOLISHING TREATED DIFFUSION COATED Nb<sub>3</sub>Sn SURFACES\*

U. Pudasaini<sup>1</sup>, G. Ereemeev<sup>2</sup>, C. E. Reece<sup>2</sup>, J. Tuggle<sup>3</sup>, M. J. Kelley<sup>1,2,3</sup>

<sup>1</sup>Applied Science Department, The College of William and Mary, Williamsburg, VA 23185, USA

<sup>2</sup>Thomas Jefferson National Accelerator Facility, Newport News, VA 23606, USA

<sup>3</sup>Virginia Polytechnic Institute and State University, Blacksburg, VA 24061, USA

## Abstract

The Nb<sub>3</sub>Sn-coated cavities aim to enhance performance and significantly reduce cost. Their fabrication involves tin vapor diffusion coating of Nb<sub>3</sub>Sn on the interior surface of a Nb cavity. Controlled removal of the first few layers to obtain a smoother and cleaner surface could be desirable to improve the high field RF performance. Our first results from the application of electropolishing and oxypolishing techniques on Nb<sub>3</sub>Sn-coated surfaces indicated reduced surface roughness, and the surface composition appeared nominally unchanged. Systematic studies explore the effect of different polishing parameters into the roughness and composition. We present the latest results from SEM/EDS and AFM studies of Nb<sub>3</sub>Sn-coated samples treated with electropolishing and oxypolishing.

## INTRODUCTION

Many decades of R&D efforts are bringing niobium SRF cavity performance close to its ultimate limit, and alternate materials are gaining attention for superior performance and cost reduction. Nb<sub>3</sub>Sn is the leading material among them now. Because of superior superconducting properties ( $T_c \sim 18.3$  K,  $H_{sh} \sim 425$  mT and  $\Delta \sim 3.1$  meV), compared to niobium, it promises better performance and higher operation temperature. Since material properties preclude bulk application, Nb<sub>3</sub>Sn-coated SRF cavities are produced by depositing a few microns thick Nb<sub>3</sub>Sn layer inside of Nb cavities using the tin vapor diffusion technique [1-3]. It develops a typical roughness on the surface after the coating deposition. Several material removal techniques (e.g. electropolishing (EP), buffer chemical polishing (BCP), oxypolishing etc). are available for niobium cavities. They are successful removing defects and contamination from the surface, and smoothing it for better performance. Similar techniques usable for Nb<sub>3</sub>Sn coated surface have not been established yet. Development of such techniques can be beneficial to reduce the roughness leading to the cleaner defect-free surfaces, which could improve the cavity performance. Despite the challenges posed by a limited amount of bimetallic material available to process, several techniques applicable to niobium were applied to Nb<sub>3</sub>Sn by limiting the process time [4-5]. Electropolishing and oxypolishing indicated some potential for controlled removal of Nb<sub>3</sub>Sn material. Following an encouraging result from electropolishing [6], we varied polishing parameters, and studied the resulting surface. Evolution of Nb<sub>3</sub>Sn surfaces

after several cycles of successive oxypolishing was studied.

## EXPERIMENTAL

### *Nb<sub>3</sub>Sn Sample Preparation*

A standard set of 10 mm × 10 mm coupons were produced from SRF grade niobium sheet, used for cavity fabrication. Each sample received ~100 μm BCP removal using a solution of 49% HF, 70% HNO<sub>3</sub> and 85% H<sub>3</sub>PO<sub>4</sub> in the ratio of 1:1:1 by volume. They were subjected to metallographic polishing, also known as nanopolishing (NP), suitable to obtain smoother substrate surfaces. These samples were then coated with Nb<sub>3</sub>Sn following the usual Nb<sub>3</sub>Sn sample coating procedure at Jefferson Lab [7]. The temperature profile included a six-hour deposition step at 1200 °C instead of the usual three hours to make the Nb<sub>3</sub>Sn coating thicker. Two sets of samples coated in two separate runs were used in this study. One of the sets show some potential tin residue on the surface.

### *Electropolishing Treatments*

The setup consisted of a polytetrafluoroethylene (PTFE) container as an electrolytic cell, aluminium cathode and the Nb<sub>3</sub>Sn-coated sample as an anode. Niobium rod was used for electrical connection to the sample, which was partly exposed to electrolytic solution during each treatment. Unlike typical electropolishing of niobium with 1:9 or 1:10 volume ratio of the mixture of 49% HF and 98% H<sub>2</sub>SO<sub>4</sub>, the volume ratio was reduced to 1:49, 2:48, 3:47 or 4:46 in electrolytic solution. Since, decreasing of HF volume ratio results in lower anodic current density, it was expected to lower the removal rate, making it suitable to process a thin layer of coating. Expected removal rate for each electrolytic solution was estimated from the anodic current density data reported before for niobium electropolishing for different ratios of acid solution [8]. Nb<sub>3</sub>Sn coated samples were treated electrochemically in each solution for estimated approximate removal of 50 nm – 500 nm. Expected removal rate was ~70, 135, 200 or 242 nm/min with 1:49, 2:48, 3:47 and 4:46 volume ratio of the mixture of 49% HF and 96% H<sub>2</sub>SO<sub>4</sub> respectively. Fixed voltage of 6.5 V was used for each treatment. The temperature of electrolyte was within 22-25 °C at the beginning, which altered 1-2 °C at the end of some experiments.

### *Oxypolishing*

Oxypolishing is one of the processes that has been applied to Nb<sub>3</sub>Sn coated cavities before [9-10]. The oxide

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layer was grown on the Nb<sub>3</sub>Sn coated sample via electrochemical anodization in 15% NH<sub>4</sub>OH solution by applying a fixed cell voltage of 30 V, and subsequently rinsed with HF to remove the oxide layer. It is expected to grow ~75 nm thick oxide layer by using thickness-voltage relation [4]. Nb<sub>3</sub>Sn coated sample was subjected to 2, 8 and 12 cycles of treatments in successive experiments for approximate expected removal of 50nm followed by additional 200 nm, and then 300 nm removal.

### Characterization

Local composition and microstructure of as-coated and electrochemically treated samples were examined by an Hitachi 4700 field emission scanning electron microscope (FE-SEM) with energy dispersive x-ray spectroscopy (EDS). The surface topographic measurement was carried out using a Digital Instruments Nanoscope IV atomic force microscope (AFM) in tapping mode using silicon tips with radius < 10 nm, resonant frequency 300 kHz and force constant 40 N/m. The scan sizes for selected samples were 50 μm × 50 μm and 10 μm × 10 μm, and 512 × 512 data points were acquired for each of 4-5 randomly selected areas. Averaged root mean square roughness (R<sub>q</sub>) will be used in this paper for roughness comparison between the samples. Standard deviation is used as an error bar. Note that, roughness varies largely among 10 μm × 10 μm scans compared to 50 μm × 50 μm scans from different locations of the same sample. This is because only a few grains captured within 10 μm × 10 μm scan, and the roughness varies with size and number of grains are captured. In the larger scans of 50 μm × 50 μm, a sufficient number of grains get captured to represent average roughness, and will be used here to interpret the roughness change following any treatment.

## RESULTS AND DISCUSSION

In the first set of experiment, a set of samples prepared in the same coating run was subjected to electropolishing in 1:49, 2:48, 3:47 EP solution for ~ 50 nm and 200 nm removal. Comparison of roughness before and after treatments is presented in Table 1. It appears that the roughness slightly increased or stayed the same following each treatment. Obtained surfaces after the EP treatment in 1:49 solutions are shown in Figure 1, see (b) and (c). Grains appeared to develop some new features, which may have increased the roughness.

Similar removal was attempted in another set of coated samples, prepared in the same coating run with 4 : 46 EP solution. The roughness reduced here in each treatment as evident in 50 μm × 50 μm scans, shown in Table 2 (left). It indicated a surface smoothing. AFM images are shown in Figure 1, see (e), (f) and (g) from these treatments. Note that the suspected tin residue disappeared after 50 nm EP in this case. Similar set of coated samples was also EPed for ~500 nm material removal in each studied acid solutions. The roughness presented in Table 2 (right) shows roughness reduction in each case. Minimum roughness was achieved with 4:46 EP solution.

Table 1: Averaged root mean square roughness (R<sub>q</sub>) of sample after ~ 50nm and 200 nm EP removal. Note that the R<sub>q</sub> value of similar untreated sample was (251±39) nm and (307±15) nm for 10 μm x 10 μm and 50 μm x 50 μm respectively.

Volume ratio of HF/H <sub>2</sub> SO <sub>4</sub>	50 nm removal		200nm removal	
	R <sub>q</sub> 10 μm x10 μm (nm)	R <sub>q</sub> 50 μm x 50μm (nm)	R <sub>q</sub> 10 μm x 10μm (nm)	R <sub>q</sub> 50 μm x 50 μm (nm)
1:49	285±64	326±7	222±25	303±29
2:48	213±35	312±21	245±23	324±13
3:47	203±17	296±16	235±27	323±10

Table 2: Surface roughness following EP treatments in 4:46 EP solution (left). Comparison of roughness following ~500 nm EP removal with different EP solutions (right).

Expected removal with 4:46 EP solution (nm)	R <sub>q</sub> 10 μm x10 μm (nm)	R <sub>q</sub> 50 μm x 50μm (nm)	Volume ratio of HF/H <sub>2</sub> SO <sub>4</sub>	500nm removal	
	R <sub>q</sub> 10 μm x 10μm (nm)	R <sub>q</sub> 50 μm x 50 μm (nm)		R <sub>q</sub> 10 μm x 10μm (nm)	R <sub>q</sub> 50 μm x 50 μm (nm)
Untreated	238±22	328±10	1:49	239±42	292±9
50	213±35	312±21	2:48	265±32	293±7
200	224±20	272±9	3:47	239±42	285±10
500	209±15	263±26	4:46	209±15	263±26

AFM images in Figure 1, (i), (j) and (k) show a Nb<sub>3</sub>Sn coated surfaces following Nb<sub>3</sub>Sn coated samples after sequential oxypolishing. Despite the reduced roughness after first oxypolishing compared to untreated sample, see Table 2, the roughness increased after second and third oxypolishing. Note that, the roughness is still less or very similar to reference as-coated sample.

Table 3: Roughness Evolution in Sequentially Oxypolished Sample

Oxypolishing	Expected Removal (nm)	R <sub>q</sub> 10 μm x10 μm (nm)	R <sub>q</sub> 50 μm x 50μm (nm)
30 V x 2	50 nm	213±12	291±7
Plus 30 V x 8	Plus 200 nm	244±47	302±12
Plus 30V x 12	Plus 300 nm	196±17	311±11

Samples were examined with SEM/EDS following each treatment. The composition of the coating was not altered following any treatment. Since the coating was fairly thick compared to removed material in any experiment, resolution of EDS may not capture the surface composition.

Surface degradation by hole formation has been reported before for oxypolishing removal corresponding to total voltages of more than 200 V [11]. No such holes were observed in our study, but irregular etched spots or features that look like residue were noticed, within grains after ~500nm EP or oxypolishing removal, as seen in on Figure 1(k) or 2.

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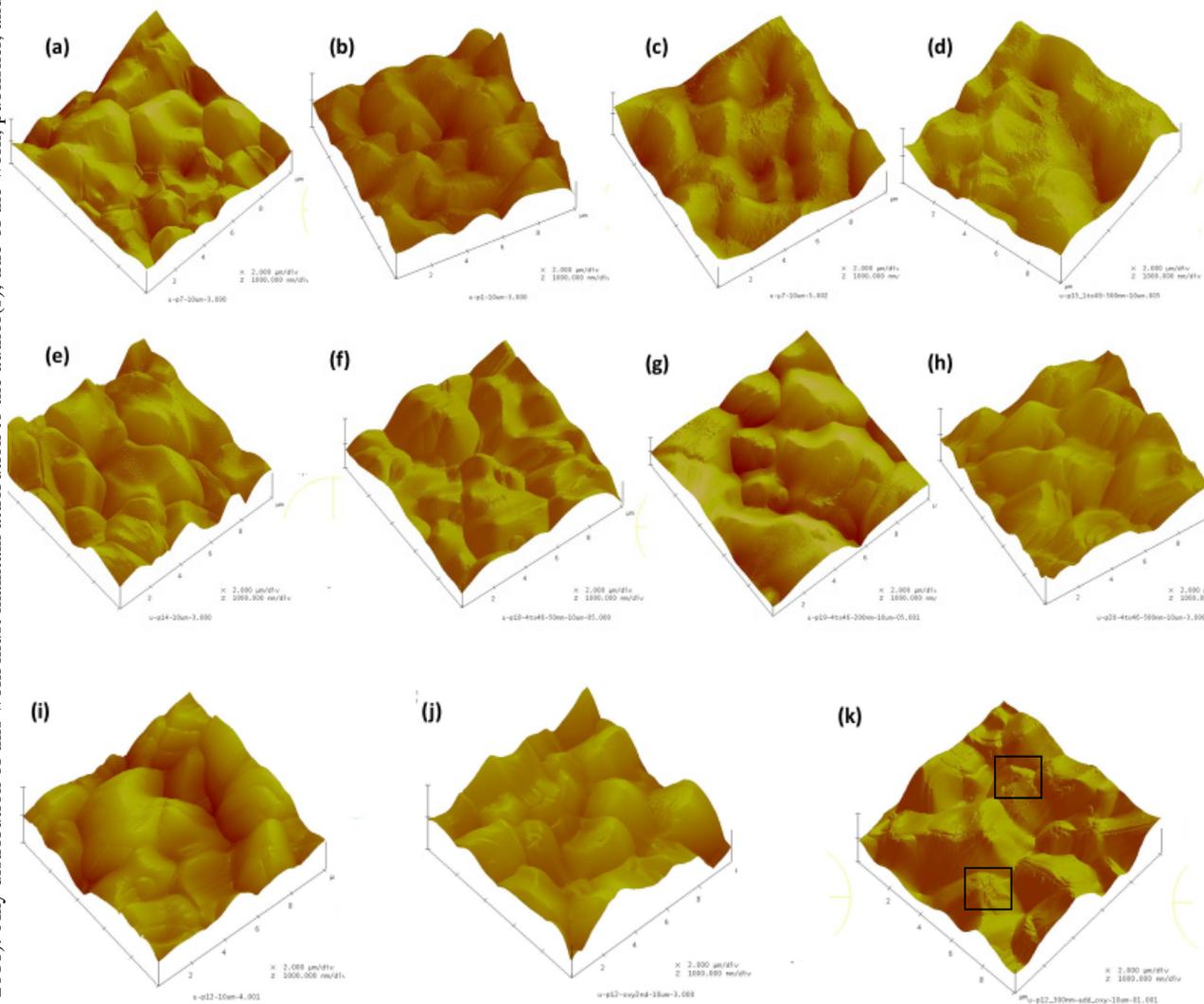


Figure 1: Topography of surfaces after electropolishing and oxypolishing treatment. (a) and (e) are as coated reference  $Nb_3Sn$  surfaces. (a), (b) and (c) were coated together, showed no tin residues. Others were from another coating run showing potential tin residues as seen in (e). (b), (c) and (d) respectively received  $\sim 50$  nm, 200nm and 500 nm EP removal in 1:49 volume ratio mixture of 96% HF and 48%  $H_2SO_4$ . (f), (g) and (h) subjected to EP for similar removal of  $\sim 50$ nm, 200 nm and 500nm in 4:46 volume ratio of 96% HF and 48%  $H_2SO_4$ . (i), (j) and (k) received 2, 8 and 12 cycle of 30 V oxypolishing for similar amount of removal successively.

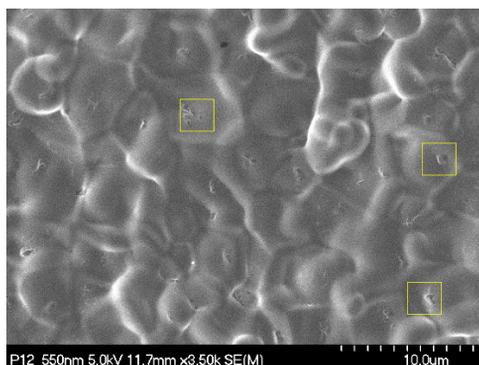


Figure 2: SEM image from sample after three successive oxypolishing ( $\sim 550$  nm removal). Note new features, like enclosed inside yellow boxes.

## SUMMARY AND FUTURE WORKS

$Nb_3Sn$  coated samples were attempted to oxypolish, or electropolish using different volume ratio of the mixture of 49% HF and 98%  $H_2SO_4$ . The data indicates conformal removal by both treatments with perhaps light smoothing. Macroroughness appeared to be consistently reduced with material removal with 4:46 EP solution, but further studies are needed to conform. Note that the standard EP solution (1:10 volume ratio) showed similar results before [6]. AFM and SEM images show irregularly etched spots or residues-like features in some sample following electrochemical treatment. Such area needed further investigations. Treated samples will be examined with XPS for possible composition degradation at the surface.

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