

ELECTROCHEMICAL FINISHING TREATMENT OF Nb₃Sn DIFFUSION-COATED NIOBIUM*

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Abstract

Nb₃Sn cavities are now routinely prepared by depositing few micron thick Nb₃Sn coatings on Nb cavities using tin vapor diffusion process. For the case of niobium there is a significant improvement after electropolishing (EP), but electrochemical finishing treatment on Nb₃Sn coatings has not been studied. Controlled removal of the first few layers could lead to a smoother and cleaner surface that is conducive to better RF performance. Several samples, which were coated with Nb₃Sn by vapor diffusion process in a JLab sample chamber, were used to explore polishing parameters, such as I-V characteristics, removal rate, topography, etc. Preliminary results from the first runs are discussed here.

INTRODUCTION

After decades of R&D efforts, the performance of SRF cavities made from niobium is approaching the fundamental limits set by the material. Nb₃Sn is a promising superconducting material ($T_c \sim 18\text{K}$ and $H_{sh} \sim 410\text{ mT}$) and has the potential to substitute niobium in SRF cavities for better performance and cost reduction [1]. It is a brittle material with thermal conductivity three orders of magnitude lower than niobium, which precludes its application as a bulk material to fabricate cavities. Nb₃Sn cavities are commonly fabricated by depositing a Nb₃Sn coating inside the Nb cavities using tin vapor diffusion technique [2-4]. Such cavities are able to achieve an accelerating gradient as high as 16 MV/m with quality factor 10^{10} at 4.2 K [4]. Degradation of RF performance beyond a certain gradient is not well understood yet. It is suspected that the roughness of an as-coated surface may play some role in such degradation. Note that Nb₃Sn develops a characteristic topography independent of substrate preparation method [5]. A typical example of such a surface is shown in Figure 1. It is thought that controlled removal of the top few layers of material could lead to better RF performance due to a smoother and cleaner surface. Material removal techniques commonly used for niobium pose several challenges for Nb₃Sn, primarily because the material available to process for the latter is only a few microns thick. Also, the response of an intermetallic compound may be dissimilar to that of a pure metal. Different material removal techniques applied for niobium were surveyed for Nb₃Sn [6-7]. It was found that buffered chemical polishing (BCP) is very reactive and etches the

surface non-uniformly within only a few seconds. Oxy-polishing and electrochemical treatments, however, did show some potential to apply to a Nb₃Sn-coated surface. Since electropolishing significantly enhances cavity performance for the case of niobium, electrochemical treatment of Nb₃Sn was explored. In this contribution, preliminary results are presented from recent first experiments.

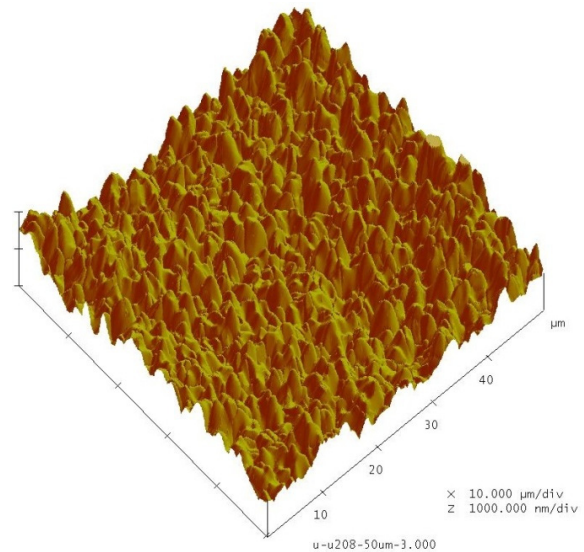


Figure 1: Typical topography of a Nb₃Sn coating on a niobium substrate.

EXPERIMENTAL

Nb₃Sn Sample Preparation

A standard set of 10 cm x 10 cm coupons and cylindrical samples with surface area 1.96 cm² were produced from high RRR sheet material of the type used for cavity fabrication. Each sample received ~ 100 microns BCP removal using a solution of 49% HF, 70% HNO₃ and 85% H₃PO₄ in the ratio of 1:1:1 by volume. These samples were then coated with the Nb₃Sn coating procedure at Jefferson Lab. A detailed description of the coating procedure is available in [5]. The temperature profile and amount of tin supplied was slightly changed to make the Nb₃Sn coating thicker. The temperature profile included a six-hour deposition step at 1200 °C instead of the usual three hours, and the initial amount of tin loading was increased from 3 mg/cm² to 4 mg/cm². A few nanopolished samples with the usual Nb₃Sn coating were also used in some experiments.

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Electrochemical Treatments

The experimental set up for electrochemical treatments consisted of a polytetrafluoroethylene (PTFE) container as an electrolytic cell, aluminium/graphite cathode and the Nb₃Sn-coated sample as an anode. A schematic of the experimental setup is shown in Figure 2. Similar to a typical electropolishing of niobium, 1:10 volume ratio of the mixture of 49% HF and 98% H₂SO₄ was used as an electrolytic solution. Since the goal of this work is to determine the possibility of electropolishing Nb₃Sn coatings, current-voltage (I-V) characteristics of the process were measured using Gamry Instruments Reference 3000 potentiostat controlled with a commercial software package.

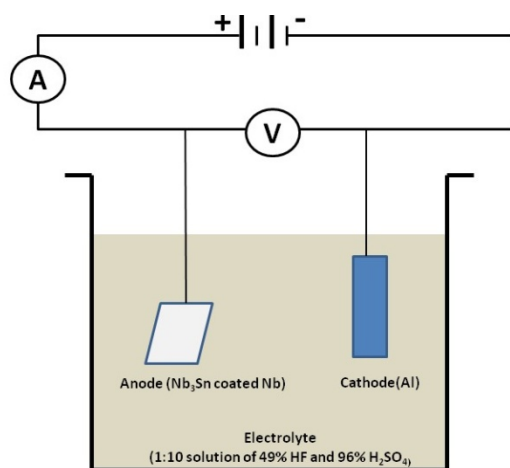


Figure 2: Experimental setup.

Following the I-V characteristics measurement, electrochemical finishing was attempted to polish Nb₃Sn-coated samples. Three samples were subjected to electropolishing for one, two or three minutes at 21°C. The temperature of electrolyte was lowered to < 6 °C by using an ice bath in the second set of experiments. Four samples were electropolished for 1, 1.5, 2 or 2.5 minutes.

Characterization

Local composition and microstructure of as-coated and electrochemically treated samples were examined by a Hitachi 4700 field emission scanning electron microscope (FE-SEM) or a Phenom ProX scanning electron microscope (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 x 50 μm and 10 μm x 10 μm, and 512 x 512 data points were acquired for each of four randomly selected areas.

RESULTS AND DISCUSSION

I-V Characteristics

The first step in assessing the I-V characteristics of Nb₃Sn-coated samples was to immerse the samples in a standard 1:10 electropolishing electrolyte solution at room temperature for either 15 or 30 minutes. Subsequent SEM examination of the samples revealed no apparent change in composition or microstructure of the surface, indicating the stability of Nb₃Sn in electropolishing solution. As shown in Figure 3, a typical I-V curve for electropolishing consists of three major regions which depend on the applied voltage [8]. The first region from V_a - V_b results in etching. The plateau between V_b and V_c is the region where the polishing effect is achieved. Higher voltages beyond V_c involve the evolution of gaseous oxygen. The region around V_b often has oscillating current.

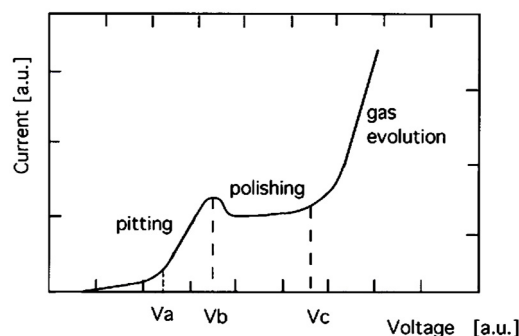


Figure 3: Typical I-V characteristics for electropolishing.

A cylindrical niobium sample or an identical Nb₃Sn-coated sample was used to measure the I-V characteristics at 21 °C. The comparison of current densities for applied voltages from 0 to 8 volts is presented in Figure 4. This measurement was limited to 8 volts in order to make sure the Nb₃Sn layer was not removed completely. Data acquisition time was 80 seconds for this measurement. As shown in figure, the both the niobium and Nb₃Sn-coated sample share similar I-V characteristics. The constant current density plateau suggests a polishing region beyond 3.5 V. SEM/EDS examination of the Nb₃Sn-coated sample following I-V characteristics measurement showed the presence of a Nb₃Sn layer. This measurement was found to be reproducible. The extended I-V characteristics measurement up to 20V appeared similar to that of Nb.

Electropolishing

Following the I-V measurement, samples U187, U199 and U202 were electropolished at 6.5 V for 1 minute, 2 minute and three minutes, respectively. The surfaces obtained for each sample following the treatments, along with as-coated sample U208 included as a reference, are shown in Figure 6. Note that as-coated sample U208 shows residual tin on the surface due to longer coating

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time and excess tin supply. Topographic modification following each treatment is evident, with a smoother appearance of treated surfaces compared to untreated surfaces. Grain boundaries are less prominent, and grain facets are less steep after each treatment. AFM measurements of roughness are tabulated in Table 1. Since the substrate was BCP treated fine-grained niobium, it could alter the root-mean-square roughness (R_q) or average roughness (R_a) because of the niobium grain boundaries inclusion or etch steps normally visible in larger scans. It appears electrochemical treatment reduced the roughness range. For example, the measured R_q from a 50 $\mu\text{m} \times 50$

μm scan area decreased from 300 - 500 nm for the as-coated sample to 225 - 350 nm after one minute of treatment, 180 - 220 nm after 2 minutes of treatment and 130 - 290 after 3 minutes of treatment. A similar trend also emerged in 10 $\mu\text{m} \times 10 \mu\text{m}$ scans, indicating significant roughness reduction. Note that the estimated rate of removal for Nb_3Sn (13.5 nm/minute per mA/cm^2) was slightly higher than niobium (14.5 nm/minute per mA/cm^2). The estimation assumes the nominal composition of Nb_3Sn , and it does not change the stoichiometry following a treatment.

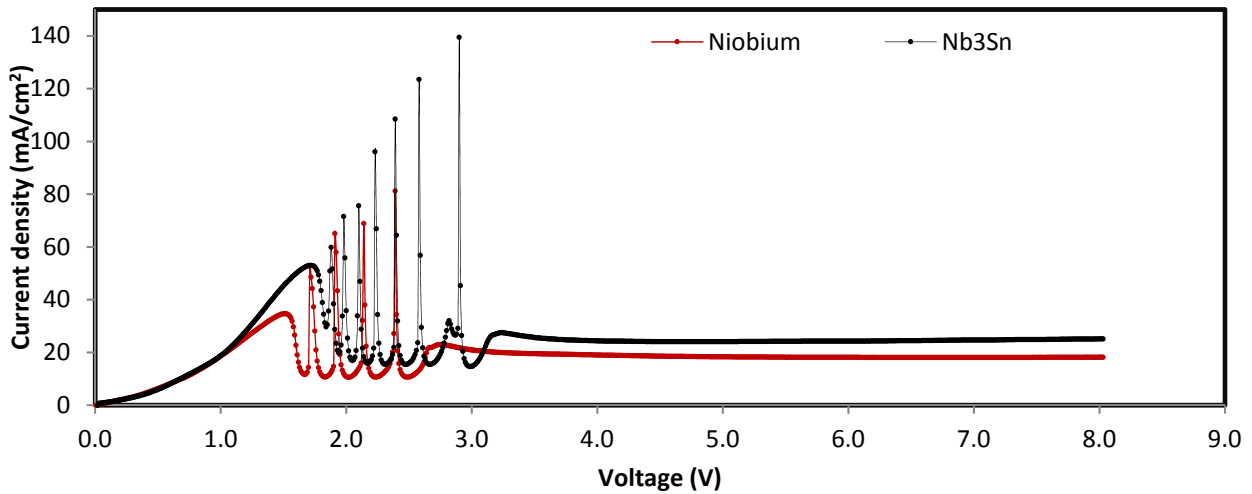


Figure 4: I-V characteristics for niobium and Nb_3Sn -coated niobium samples.

Table 1: Roughness of Sample before and after Electrochemical Treatment at 21 °C

	U208: As coated-No EP		U187 EP 60 s at 21°C		U199 EP 120 s at 21°C		U202 EP 180 s at 21°C	
	R_q (nm)	R_s (nm)	R_q (nm)	R_s (nm)	R_q (nm)	R_s (nm)	R_q (nm)	R_s (nm)
50 $\mu\text{m} \times 50 \mu\text{m}$	296	238	225	179	179	140	286	228
	340	269	310	248	199	157	183	147
	285	228	261	205	159	125	129	100
	474	382	346	254	220	175	150	111
10 $\mu\text{m} \times 10 \mu\text{m}$	162	139	112	91	80	63	144	110
	224	180	142	114	133	104	156	124
	168	141	175	139	88	67	103	77
	177	149	117	93	108	86	81	62

In the second set of experiments, the electrolytic solution was cooled to 1 °C in an ice bath in order to lower the current density. Samples U107, U152, U208 and U214 were electropolished with an applied voltage of 6.5 V for 1, 1.5, 2 and 2.5 minutes at 1°C, 3°C, 4°C and 5°C, respectively. Note that samples U208 and U214 were coated in the same experimental run as U187, U199 and U202. The substrates of U107 and U152 were nanopolished prior to coating and were subjected to the usual coating protocol. Nanopolished substrates are ad-

vantageous because roughness can be measured more precisely since the coating is deposited onto a uniformly smooth surface. In contrast to the samples that received BCP treatment, there appears to be no significant roughness variation location to location in coated nanopolished samples. Figure 7 shows AFM images of as-coated and treated samples. Treated surfaces appeared smoother than as-coated surface like first set of experiments. As shown in Table 2, the roughness measurements from the two scan sizes are similar. Comparing nanopolished samples, the range of measured values for R_q of a 50 $\mu\text{m} \times 50 \mu\text{m}$ scan decreases from 175 - 198 nm for the as-coated sample to 109 - 131 nm after 1.5 minutes of electropolishing. Significant roughness reduction was also observed in U208 and U214 following the treatment.

The power spectral density (PSD) was calculated following the same method as in [9] by Fourier transform of the scan data. PSD was calculated for 3 of each 50 $\mu\text{m} \times 50 \mu\text{m}$ scans from samples prepared in identical conditions following the treatment. Obtained log-log plot is shown in Figure 5. Note that the area under PSD curve corresponds directly to root-mean-square (RMS) roughness. Reduction of roughness is normally evident for each spatial frequency, but some scans had some deviation.

Each sample was examined using EDS following the experiment. Following electrochemical treatment, 24 ± 1 atomic percent tin was found in each sample, indicating no significant change in composition. Note that the lateral and depth resolution of EDS is on the order of a micron,

so slight changes in composition at the surface may not be accounted for. A residue on the surface of some samples was observed following treatment. Although EDS analy-

sis of these features indicated the presence of carbon, the source of the residue has not yet been determined.

Table 2: Roughness of Sample before and after Electrochemical Treatment < 6 °C

	U107: As coated - No EP (nanopolished substrate)		U107 EP 60 s at 1 °C (nanopolished substrate)		U152 EP 90 s at 3 °C (nanopolished substrate)		U208 EP 120 s at 4 °C		U214 EP 150 s at 5 °C	
	R _q (nm)	R _a (nm)	R _q (nm)	R _a (nm)	R _q (nm)	R _a (nm)	R _q (nm)	R _a (nm)	R _q (nm)	R _a (nm)
50 μm x 50 μm	196	156	148	118	109	83	242	189	182	145
	192	154	87	68	109	87	273	226	157	123
	175	139	142	112	111	86	306	293	162	129
	198	160			131	105	237	188		
10 μm x 10 μm	194	156	130	104	109	83	131	100	102	81
	197	157	57	45	110	88	128	103	94	76
	164	129	123	100	111	86	104	81	75	60
	181	142			97	77	148	118		

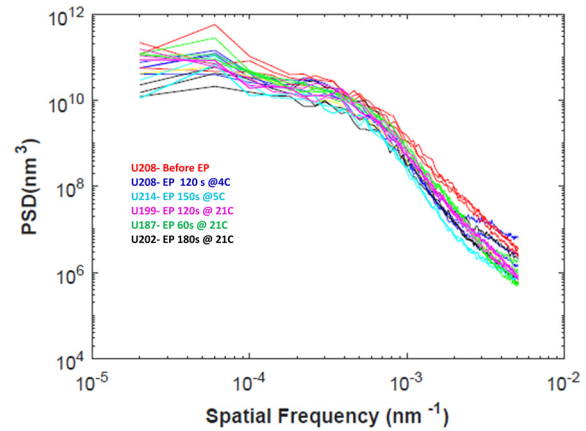


Figure 5: Comparison of PSDs from Nb₃Sn coated sample before and after EP. Note that all the samples were coated in the same run.

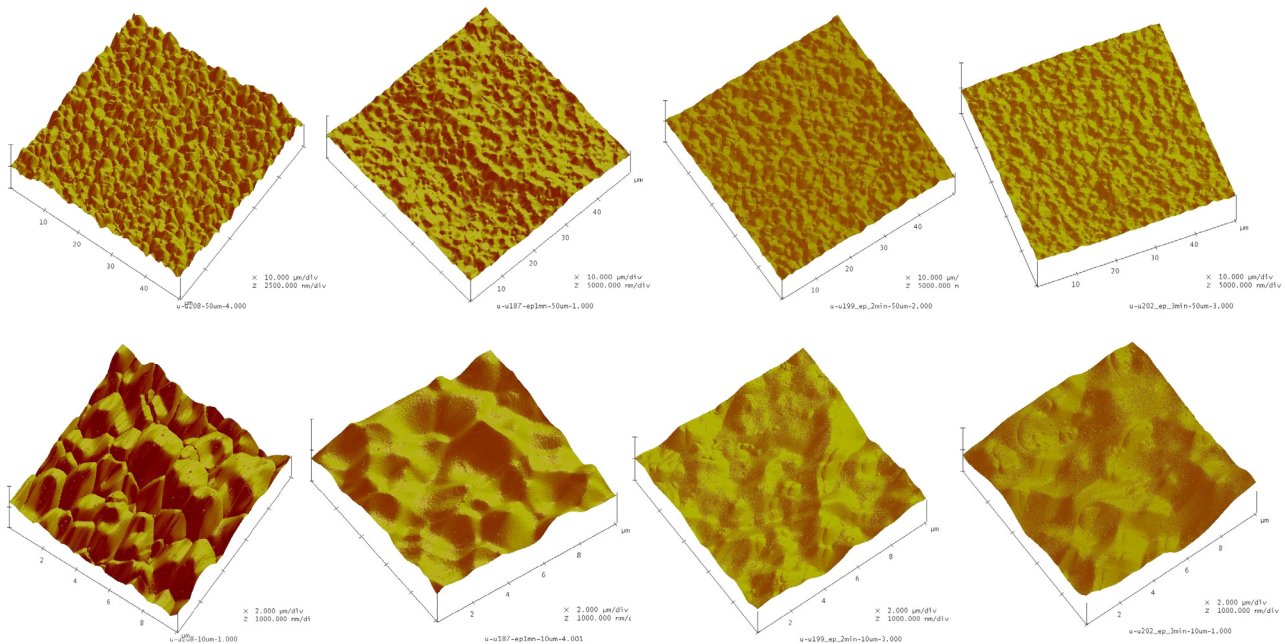


Figure 6: Nb₃Sn-coated samples before and after electrochemical treatment at 21°C. Images obtained from as-coated sample U208 are shown in first column. Topography of samples U187, U199 and U202 which received 1, 2 and 3 minutes of treatments are shown in second, third and the last column respectively. First rows of images represent 50 μm x 50 μm scan areas whereas second rows images represent 10 μm x 10 μm scan areas.

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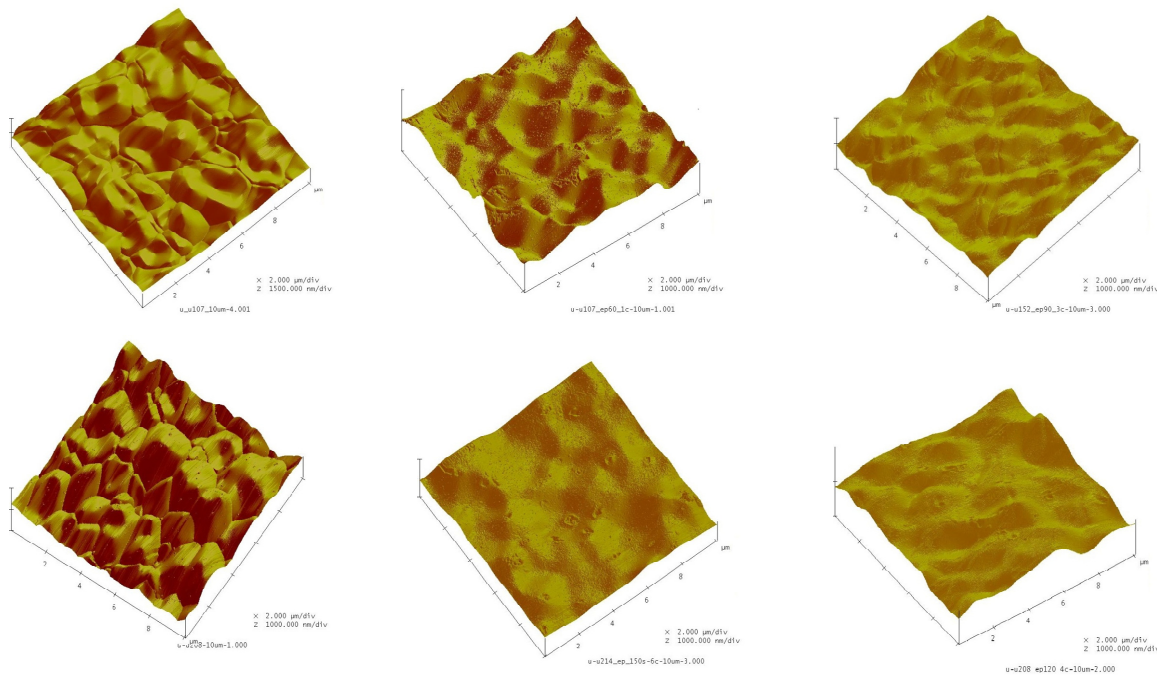


Figure 7: Nb₃Sn-coated samples before and after electrochemical treatment at < 6 °C. Images obtained from as-coated samples U107 and U208 are shown in first column. Images in first row are from the samples that were coated on nanopolished substrates. Samples U107, U152, U208 and U214 received 1, 1.5 and 2 and 2.5 minutes of treatments, respectively. Images represent 10 μm x 10 μm scan areas.

SUMMARY AND FUTURE WORK

Electrochemical finishing treatments similar to the electropolishing of niobium were applied to Nb₃Sn-coated niobium samples. The examined topography and roughness of coated coupon samples before and after the application of electrochemical treatment shows a clear polishing action of the surface. As opposed to BCP treatment, the material removal rate is more controllable for electropolishing and the material removal is more uniform. The actual mechanism of polishing is not yet understood, but observed current-voltage characteristics suggest a mass transport limited process similar to niobium, and needs further research. Surface sensitive XPS and AES elemental measurements are in progress to probe surface features, and post-treatment elemental composition of the surface. Plans are also under way to change the composition of the acid solution in order to lower the removal rate further, providing more time to stabilize the current density. If successful, electrochemical finishing treatment will be attempted into a Nb₃Sn coated niobium cavity.

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