

SURFACE STUDIES OF Nb₃Sn COATED SAMPLES PREPARED UNDER DIFFERENT COATING CONDITIONS*

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Abstract

The promise of better performance and significant cost reduction make Nb₃Sn-coated Nb SRF cavities an attractive option when compared to traditional Nb SRF cavities. Historically, the vapor diffusion technique for coating Nb cavities with Nb₃Sn has proven to be the most successful, and is currently practiced in several research facilities with minor variations. Using modern characterization tools, we examined the Nb₃Sn coating prepared in different systems and/or under different conditions. Identically prepared high RRR (~300) Nb samples were coated using existing standard protocols at different coating facilities. The microstructure and composition of Nb₃Sn coatings were found to be similar when examined with scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS). Atomic force microscopy (AFM) was performed on each sample and the topographies of the samples were then compared in terms of power spectral densities (PSDs). Secondary ion mass spectrometry (SIMS) depth profiles revealed trace amounts of Ti in some of the samples.

INTRODUCTION

Presently, Nb₃Sn is the front running candidate for replacing Nb in SRF accelerator cavities and as such, it has become an active topic of research and development efforts [1-4]. The goal of these efforts is to more fully understand both the limitations of Nb₃Sn and methods by which to optimize its SRF cavity performance enhancing capabilities. Since the application of this material is limited to the form of a coating, SRF cavities should be prepared by depositing Nb₃Sn of 2-3 micron thickness inside of accelerating structures. The tin vapor diffusion technique has been the leading technique for fabricating Nb₃Sn-coated Nb cavities since the 1970's [5-7]. The typical coating procedure involves vaporizing both tin and tin chloride inside an ultra-high vacuum (UHV) furnace, where they interact with a Nb substrate to form the Nb₃Sn coating. The temperature profile inside the furnace often includes two plateaus. The first plateau at about 500 °C is known as the nucleation step, where tin chloride is evaporated and creates early tin deposition sites. During the second plateau at about 1200 °C, or the deposition step, tin is transported to the substrate where

Nb₃Sn is subsequently formed. The exact mechanism for the Nb₃Sn formation is not well understood. The importance of understanding the effects of varying coating parameters (such as nucleation time and temperature, deposition time and temperature, and the amounts of tin and tin chloride vaporized) is paramount for controlling and optimizing the final coating structure. Several experiments were performed in order to investigate the effects of varying coating process parameters on the kinetics and growth of the Nb₃Sn coating. In this contribution, an analysis of coatings produced using a number of different coating process parameter combinations are reported.

VARIATION OF NUCLEATION PROFILE

The current Nb₃Sn coating protocol in practice at different research facilities includes a nucleation step at a low temperature plateau of 500 °C for 1 - 5 hours. The purpose of this step is to generate tin enriched Nb-Sn nucleation sites on the Nb substrate through evaporation and decomposition of tin chloride. Nucleation step was evolved to prevent non-uniform and incomplete layers of Nb₃Sn from early coating experiments [5]. Recent surface studies following nucleation steps with different process parameter combinations show that, in general, both a tin film and a distribution of tin particles cover the Nb substrate surface [8]. However, variation in duration and temperature of the nucleation step, as well as the amount of tin chloride utilized, produced differences in the surfaces. A systematic set of coating experiments was performed in order to determine the effect of varying nucleation parameters on the final Nb₃Sn coatings. In each case, the nucleation step was followed by a three-hour deposition step at 1200 °C with 1 g (~2 - 3 mg/cm²) of tin and an equal amount of tin chloride. The chemical composition and microstructure of the final Nb₃Sn coatings were examined using SEM/EDS. Figure 1 shows that no significant differences in the final coatings were observed for three distinct nucleation temperature-duration profiles. This suggests that the properties of the final Nb₃Sn coating are instead dominated by the higher temperature, tin-rich deposition step.

A set of nanopolished Nb samples were pre-nucleated (300 - 500 °C for 1 to 5 hours) using typical amounts of tin and tin chloride. Subsequent to atmospheric exposure, the samples were subjected to the standard coating procedure. SEM/EDS examination showed that coatings do not depend significantly on pre-nucleation history. The chemical composition of the coating for each sample demonstrated usual ~24 atomic % of Sn. A comparison of

*Partially authored by Jefferson Science Associates under contract no. DEAC0506OR23177. Work at College of William & Mary supported by Office of High Energy Physics under grant SC0014475. This material is based upon work supported by the U.S. Department of Energy, Office of Science, Office of Nuclear Physics.

coatings from pre-nucleated samples with coatings from samples that were not pre-nucleated (referred to hereafter as “regular” samples), all other process parameters equal, show slightly smaller grain sizes in pre-nucleated samples, see Figure 2. From SEM images, the coating on pre-nucleated samples appears flatter than the coating from a regular sample. AFM examination of sample U74 revealed a root mean square roughness (r_q) of only 70 nm for 50 $\mu\text{m} \times 50 \mu\text{m}$ scans compared to a coated regular sample that normally exhibits average r_q value 100 - 150 nm, depending on grain size.

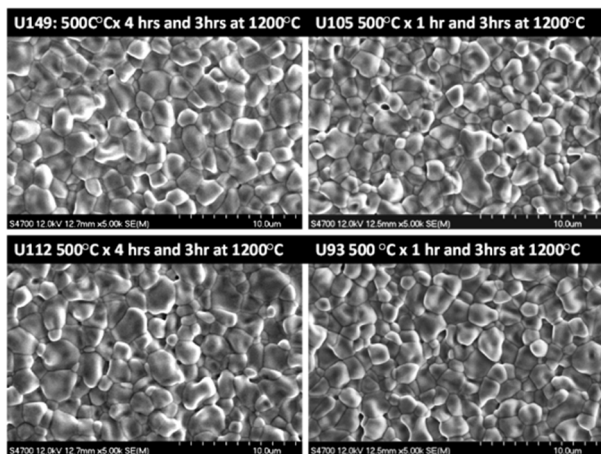


Figure 1: SEM images of Nb_3Sn -coated samples prepared with different nucleation temperature-duration profiles.

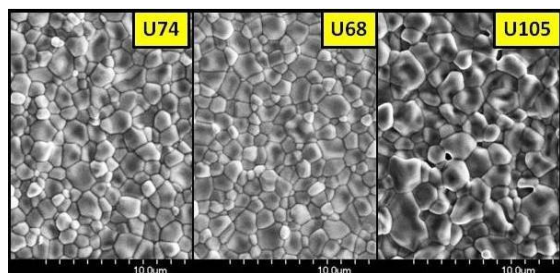


Figure 2: Coatings produced on pre-nucleated and regular Nb samples. U74 and U68 were pre-nucleated at 400 °C for 1 hour and 300 °C for 4 hours, respectively. U105 is regular coated sample.

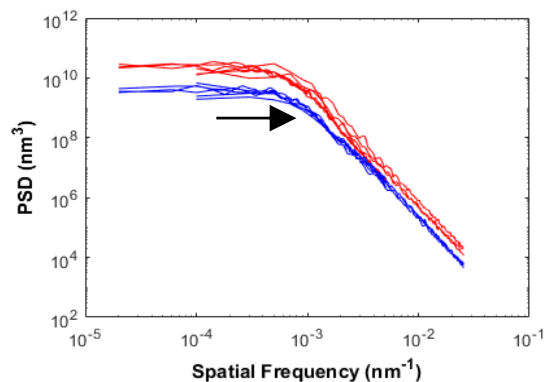


Figure 3: PSD comparison of coated sample with pre-nucleated substrate U74 and regular substrate U153. Note

that data obtained from 50 $\mu\text{m} \times 50 \mu\text{m}$ and 10 $\mu\text{m} \times 10 \mu\text{m}$ scan sizes are plotted together.

A comparison of power spectral densities (PSD) obtained from of pre-nucleated sample U74 and regular sample U153 is shown in Figure 3. Since the area under the PSD gives the square of root mean square roughness, it can be clearly seen that the roughness of sample U74 lower than that of U153.

COATING WITH LOW AMOUNT OF TIN

Existing Nb_3Sn coating protocols include loading tin into the UHV furnace sample chamber along with the Nb samples/cavity before vacuum pumping. The amount of tin provided is normally more than what would be consumed during the coating process. While coating facilities at Cornell University and Fermilab use an open crucible for tin loadings, at Jefferson Lab we supply the required amount of tin by packaging it inside Nb foil [9-11]. The amount of tin consumed during the coating process is monitored by weighing the tin packages before and after the experiment. It was found that the amount of tin evaporated during the experiments was not consistent in some experiments, and it was suspected that the tin may have been packaged too tightly in the Nb foil in some cases, causing less evaporation than intended. In this section, some instances of coatings observed in experiments with low tin evaporation are discussed.

Figure 4 shows SEM images of two Nb_3Sn coatings obtained from experiments with only 12 and 17 % tin consumption during the coating process. For the case of 12 % tin consumption, where a 1-hour nucleation step at 400 °C and a 3-hour deposition step at 1200 °C were performed, thread-like structures developed on the surface with few grain boundaries (not visible in the image). For the case of 17 % tin consumption, however, where a 4-hour nucleation step at 500 °C and a 3-hour deposition step at 1200 °C were performed, a patchy coating with relatively small grain sizes was observed. In both case, EDS analysis showed ~ 20 atomic % of tin, indicating a thin layer of deposited coating. Note that for a similar experimental setup with supplied tin of ~ 2 mg/cm^2 , the typical expectation for tin consumption is around 40 %. The Nb_3Sn coatings that were obtained when these experiments were later repeated for usual amount of tin evaporation are shown in Figure 1.

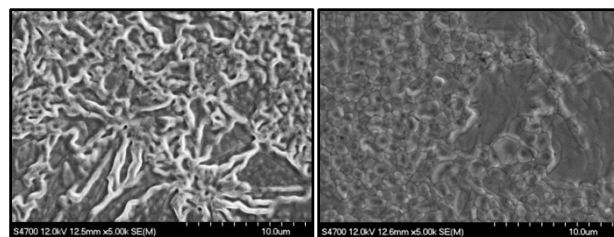


Figure 4: Coating obtained with 12 % (left) and 17 % (right) of supplied tin consumption during the coating process.

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Similar results were obtained during an examination of a sample that fell from the shelf of the sample chamber onto the Nb foil covering the bottom end of the chamber. Various locations on the bottom side of the fallen sample were examined from the edge to the center. A coating gradient was formed which appeared to depend on the amount of tin supplied at each location. The coating near the edge shows small grains with occasional patches. At ~ 2.5 mm away from the edge, the coating had thread-like structures. EDS analysis revealed ~ 20 atomic % tin. At 5 mm away from the sample edge, close to the center, no structures were present. Only Nb was detected with EDS. SEM images representing coating from edge to center is shown in Figure 5, which appears to be consistent with Figure 3.

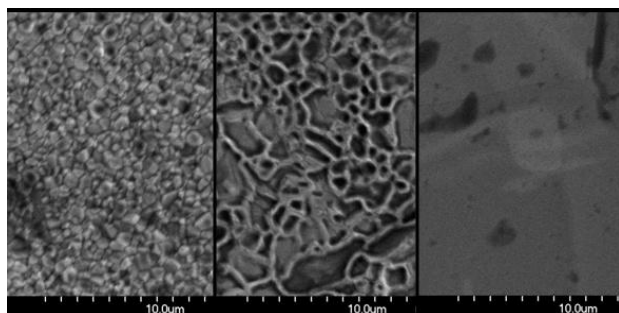


Figure 5: Coating developed in sample U16 that fell from the sample holder during coating. Images were taken from 1 mm, 2.5 mm, and 5 mm from the edge.

COATING WITH ONLY TIN CHLORIDE

SnCl_2 is used as a nucleation agent in a typical Nb_3Sn coating process. It is evident that through evaporation of SnCl_2 , tin particles are deposited and a thin tin film covers the Nb surface at low temperature of about 500 °C [8]. Even so, experiments have never been conducted to investigate the coatings formed at elevated temperature in the absence of additional supplied tin. The coverage and microstructure of such a surface can help inform the evolution of a typical coating process. Two grams (~ 4 mg/cm^2) of SnCl_2 were used in a coating experiment with a temperature profile that included a nucleation step of 5 hours at 500 °C and a deposition step of 3 hours at 1200 °C. One of the three Nb coupon samples present in this experiment were anodized. Sample anodization was performed in a 15 % NH_4OH solution with a 40 V DC power supply. The inclusion of an anodized sample is related to ongoing nucleation studies that we plan to report elsewhere at a later time. The surfaces of the resultant Nb_3Sn coatings were examined with SEM/EDS, see Figure 6. The sample that was not anodized exhibited patchy areas and elongated grains, while the anodized sample appeared to have a more uniformly coated surface that was free of patches. In both cases the average grain size was ~ 250 nm. The chemical composition of well-coated areas of the surface contain about 21 ± 1 atomic % tin, but in patchy areas only 14 ± 3 atomic % of tin is present. The discrepancy in tin composition from nominal Nb_3Sn composition may be due to the fact that

the thickness of the tin coating was much less than the depth resolution of EDS, which is on the order of microns. Patchy regions are assumed to have a considerably thinner coating in comparison to well-coated areas.

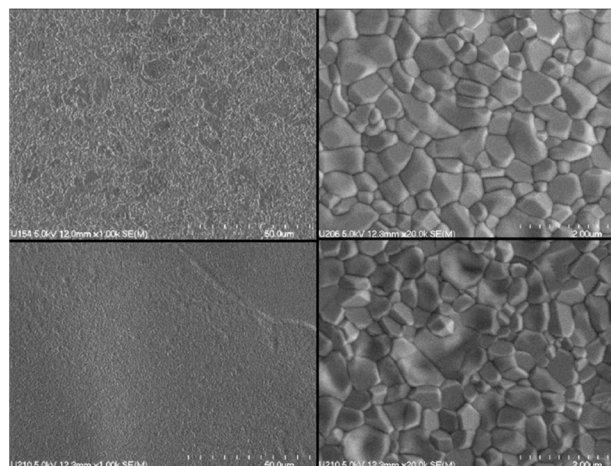


Figure 6: Nb_3Sn coating grown with only SnCl_2 . Images on the first row were from a regular Nb samples. Surfaces obtained on an anodized sample are shown in the second row. Note some patchy areas (dark areas) are present in the Nb sample that was not anodized (top left).

This experiment demonstrates the importance of the application of tin chloride. Deposition of an anodization layer appears to help to distribute tin more uniformly during nucleation. It is believed that a uniform distribution of nucleated tin particles leads to a more uniform final coating.

INTERRUPTION EXPERIMENTS

The coating process was interrupted at different points during the deposition stage in an attempt to understand process specific growth dynamics of Nb_3Sn coatings. Results from a set of experiments where the standard coating procedure (1 hour of nucleation at 500 °C and 3 hours of deposition at 1200 °C) was interrupted after 1 minute and 1 hour of deposition were previously reported [11]. A similar set of experiments were run again, but with no SnCl_2 . Only tin was supplied. Each experiment featured one anodized, one BCP treated sample and one nanopolished sample. The anodized sample was included following the interesting result from coating experiment with only SnCl_2 . Representative SEM images from the sample that was subjected to BCP treatment prior to coating are shown in Figure 7. Evidently grain growth occurs rapidly and, for the most part, in an equiaxed manner during the first five minutes of deposition. Although no patches were observed in the BCP treated sample after 5 minutes at 1200 °C, some did appear after one hour (not shown).

Patchy areas were present in the Nb_3Sn coating of the nanopolished sample at 5 minutes, 1 hour, and 3 hours at 1200 °C, see Figure 8. Nanopolished substrates are found

to be more prone to patchy areas than BCP treated substrates.

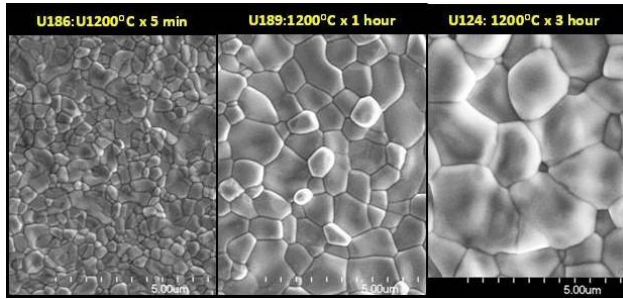


Figure 7: Coating obtained on a Nb substrate subjected to BCP treatment, without tin chloride.

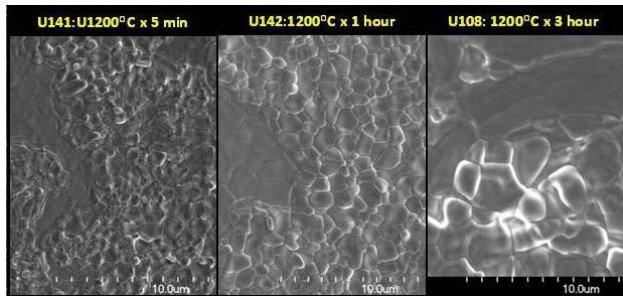


Figure 8: Nb₃Sn coating obtained on a nanopolished substrate without SnCl₂.

Anodized samples demonstrated a uniform Nb₃Sn coating with equiaxed grain formation after both interruption times of 5 minutes and 1 hour at 1200 °C as shown in Figure 9. No patches were present at either time. Results obtained with anodized sample coated with only Sn or SnCl₂ both appears to be consistent with recent results from other researchers at Cornell where they coated samples using both Sn and SnCl₂ together [12].

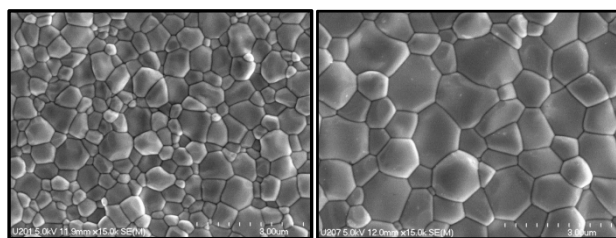


Figure 9: Nb₃Sn coating obtained on an anodized substrate after 5 minutes (left) and 1 hour (right) without SnCl₂.

SAMPLES COATED AT CORNELL UNIVERSITY AND JEFFERSON LAB

Despite the fact that the tin vapor diffusion technique is common to both facilities, the coating protocol at Cornell University is slightly different than the protocol at Jefferson Lab. Detailed descriptions are discussed elsewhere [2] and [10]. Whereas the Jefferson Lab furnace maintains both the tin source and the Nb substrate at the same temperature, the Cornell heating system is able to hold the tin source at a higher temperature than the substrate. The typical Cornell coating process includes a

5-hour nucleation step at 500 °C followed by temperature ramping of the substrate to the coating temperature of 1100 °C. The temperature of the tin source simultaneously undergoes a separate ramping such that the temperature of tin reaches 1250 °C at the same time the Nb reaches 1100 °C. After one hour, heating of the tin source terminates while the substrate temperature is maintained at the coating temperature for one additional hour. In contrast, the Jefferson Lab coating process consists of a 1-hour nucleation step at 500 °C followed by a 3-hour deposition step at 1200 °C, Jefferson lab also uses two orders of magnitude more tin chloride per unit area than Cornell.

Samples coated at both facilities were examined using SEM/EDS, AFM and SIMS. Coupon samples obtained from Cornell served as witness samples and were coated alongside cavity during the cavity coating. Samples from each facility were subsequently examined with SEM/EDS and each exhibited uniform coatings with a chemical composition of ~ 24 atomic % tin. As shown in Figure 10, while the grain structures of the Nb₃Sn deposited onto samples coated at Cornell and Jefferson Lab appear similar, there is a marked distinction in roughness produced by the different coating procedures.

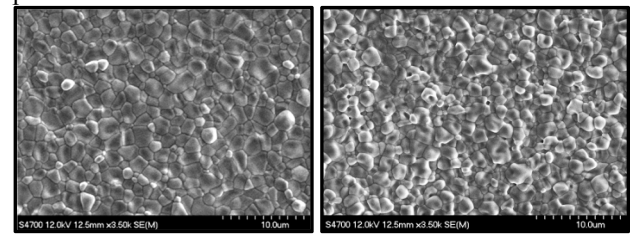


Figure 10: Nb₃Sn coated surface from RDT2 OC5 coated at Cornell University (left) and U129 coated at Jefferson lab (right). Both samples were BCP treated before coating.

AFM analysis was performed on Cornell sample RDT4 OC5 and Jefferson Lab sample U129. Representative topography of each sample is shown in Figure 11.

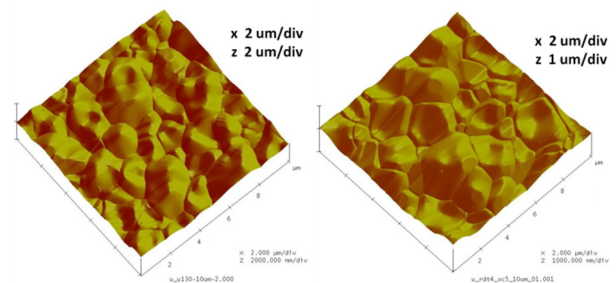


Figure 11: Topography of sample coated at Cornell (right) and Jlab (left).

The roughness of each sample surface was compared in terms of the power spectral densities (PSD) from surface height data obtained from AFM scans of 50 µm x 50 µm, 10 µm x 10 µm and 5 µm x 5 µm sized areas from four randomly selected areas from each sample. The log-log

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plot of calculated PSD is shown in Figure 12. It can be seen that the roughness of the Nb₃Sn coating produced by Jefferson Lab is greater than the roughness of the Nb₃Sn coating obtained at Cornell.

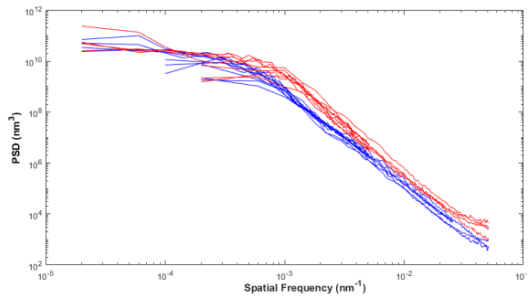


Figure 12: PSD comparison of samples coated at Cornell (blue) and Jefferson Lab (red). Note that data obtained from different scan sizes are plotted together.

Nb₃Sn-coated samples from both facilities (U4 and B19 from Jefferson Lab, M2 and RDT4 OC5 from Cornell) were also analyzed by SIMS with a CAMECA IMS7fGEO magnetic sector instrument for possible sources of trace contamination in the coatings. A detailed description of the data collection and analysis is explained in [13]. A SIMS depth profile showed the presence of carbon and oxygen on the surface of the coatings but these elements were not detected deeper within the Nb₃Sn layer. Even though significantly more tin chloride is used during the coating of Nb₃Sn at Jefferson Lab, no chlorine was detected. On the other hand, titanium was found in Jefferson Lab samples. Because the depth profile of titanium is similar to that of tin, it is speculated that it may have diffused during the coating process. From a comparison of the tin and titanium depth profiles in Figure 13, it is clear that the Jefferson Lab sample contained a significantly higher level of titanium.

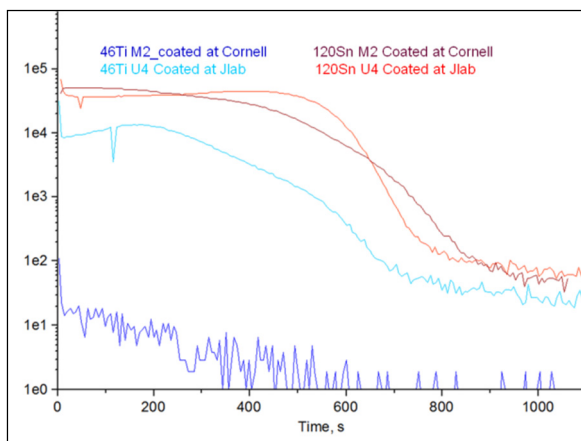


Figure 13: SIMS depth profile of Ti and Sn.

One explanation for the source of titanium contamination is leftover tungsten inert gas (TIG) weld spots in the sample chamber flanges. Another possibility is that titanium contamination originated from cavities with Nb - Ti flanges. These issues were addressed during

a recent upgrade of the Jefferson Lab coating system by commissioning a new insert and sample chamber fabricated entirely from niobium [14]. A SIMS analysis of samples recently coated at Jefferson Lab show that titanium levels are now comparable to the levels of Cornell sample M2 shown in Figure 14. Low levels of titanium appearing in these samples could be traces from past treatments done in the same furnace, but a more thorough investigation is required.

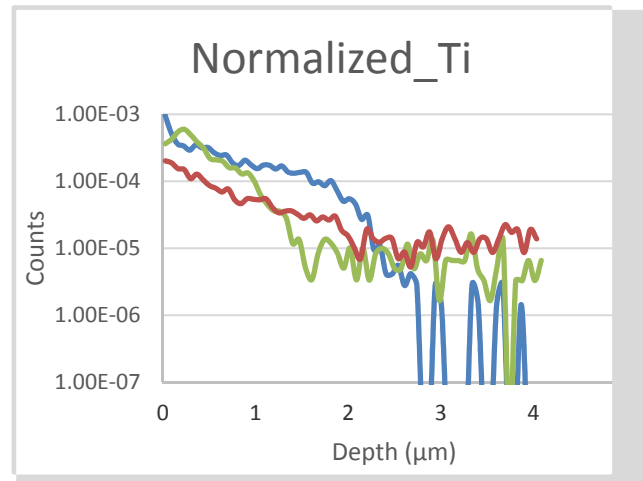


Figure 14: Depth profile of normalized Ti values. The ratio of Ti to Nb signal was taken on a point by point basis and multiplied by 100 for comparison. Note that the sample coated at Cornell (red) and the two samples coated at Jefferson Lab (green and blue) have comparable levels of titanium.

SUMMARY

Nb₃Sn coatings prepared under different conditions were discussed. SEM/EDS analysis did not show any significant changes in chemical composition or microstructure of the final coating with variation in nucleation process parameters. Complete coating with only SnCl₂ resulted in Nb₃Sn coatings, which included some patchy regions. Examination of coatings resulted in by low tin consumption during the coating were presented. Coating interruption experiment featuring anodized, non-anodized, BCP treated and nanopolished sample were reported. Anodized sample had developed more uniform coating compared to regular samples very early at the beginning of deposition temperature during the coating with only tin. It also developed more uniform coating with complete coverage when coated with only SnCl₂. Similar analysis of samples coated at Jefferson Lab and Cornell University were presented. Despite some variation in roughness, the Nb₃Sn coatings prepared in both facilities appeared similar.

ACKNOWLEDGEMENTS

We are very grateful to Matthias Liepe, Daniel Hall and Ryan Porter from Cornell University for preparing and providing Nb₃Sn coated samples. We thank Olga Trifimova at William and Mary Applied Research Center

for her continuous help for AFM characterization. SIMS analysis was done at Nanoscale Characterization and Fabrication Laboratory (NCFL) at Virginia Tech.

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