

LOCAL COMPOSITION AND TOPOGRAPHY OF Nb₃Sn DIFFUSION COATINGS ON NIOBIUM *

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Abstract

The potential for energy savings and for increased gradient continues to bring attention to Nb₃Sn-coated niobium as a future SRF cavity technology. We prepared these materials by vapor diffusion coating on polycrystalline and single crystal niobium. The effect of changing substrate preparation, coating parameters and post-treatment were examined by AFM and SEM/EDS. The AFM data were analyzed in terms of power spectral density (PSD). We found little effect of pre-coating topography on the result. The PSD's show some surprising kinship to those obtained from BCP-treated surfaces. SEM/EDS revealed no composition non-uniformities at the micron scale.

INTRODUCTION

Nb₃Sn is a superconducting material with a critical temperature and predicted superheating field nearly twice that of niobium. Accordingly, Nb₃Sn has the potential to achieve superior performance both in terms of quality factor and accelerating gradient resulting in significant reduction in both initial and operating costs.

Research on Nb₃Sn started in 1970's as a promising alternate material for SRF application. Siemens AG and University of Wuppertal took the lead. They developed a diffusion coating recipe, and successfully fabricated Nb₃Sn cavities. Operating at 4.2K, these cavities exhibited a quality factor more than 10¹⁰ up to an accelerating gradient approaching 5 MV/m, but then suffered a precipitous drop [1]. The reason was never firmly established, but it was speculated that it might be an implicit property of Nb₃Sn. Continuous improvement of niobium cavity performance and discovery of high temperature superconducting materials diverted attention from Nb₃Sn research. All the research activities fell off by the end of 1990's until Cornell started a Nb₃Sn development program in 2009. Their recent results from diffusion coated cavities are free from sharp drop of quality factor for accelerating gradient more than 10 MV/m. [2]. It revived hope of Nb₃Sn application for future accelerators once again.

A research program was initiated at Jlab recently to develop Nb₃Sn coated cavities. It is based on tin diffusion coating of niobium, which is the method of choice of most research institutions so far [1–3]. The goal is to determine

the process parameters to obtain high-performing Nb₃Sn coated niobium cavities by materials and RF studies.

It is known that Nb₃Sn is the equilibrium phase within its composition range, 18%-25%, and that the superconducting properties degrade with decreasing tin content. It is very important to obtain a deeper understanding of how the coating process controls the coating's structure and composition, and how these control performance, showing the path to better performance. Nb₃Sn samples were prepared via tin diffusion to validate the prepared coatings. Results from a study of Nb₃Sn coated samples are presented here. The focus is to examine the composition and topography of prepared coatings and its variation.

SAMPLE PREPARATION

Materials

The substrate samples used here were 10 mm × 10 mm niobium coupons produced by EDM cutting 3 mm thick, high RRR sheet material of the type used for cavity fabrication at Jlab. These were further processed.

- The first set of samples was prepared by metallographic polishing, also known as nanopolishing (NP) at Micron Analytical Inc.
- The second set of samples was subjected to buffered chemical polishing (BCP) using a solution of 49% HF, 70% HNO₃ and 85% H₃PO₄ in the ratio of 1:1:2 by volume for 14 minutes at room temperature, expected to remove about 30-40 μm.
- The third set of samples received electropolishing (EP) using a 1:9 mixture of 49% HF and 96% H₂SO₄ for one hour at room temperature, removed about 30-40 μm. Some of the samples in this set had been subjected to centrifugal barrel polishing (CBP) prior EP.
- Other samples were only degreased with Micro90 for 15 minutes and then rinsed with deionized water.

Some samples obtained by cutting a Nb₃Sn-coated cavity were also examined. It was the same cavity coated for commissioning of the Nb₃Sn cavity vapor deposition system at Jlab [3].

Nb₃Sn Coating

The Nb₃Sn cavity deposition system commissioned recently was used for coupon coating. A detailed description of deposition system is available in [3]. We fabricated a new sample chamber for sample coating. Required tin and tin chloride were packaged in niobium foils. One package (1 gm) of tin and two packages (2×0.5 gm) of tin chloride were placed on the floor of the sample chamber on the niobium foil

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which covered the bottom flange (see Fig. 1). The top flange of the sample chamber was also covered with niobium foil after mounting niobium samples inside the chamber. The set up was performed in the clean room to avoid contamination. It was then installed into the deposition system and pumped down overnight. The heating process was initiated



Figure 1: Sample chamber, samples, tin and tin chloride packages, and niobium foils before set up.

the next day. Temperature and pressure profiles during the coating process are shown in Fig. 2. The heating profile was similar to the one used in Jlab for cavity coating, it followed Wuppertal recipe with some modification. The furnace was initially heated by ramping up the temperature at a rate of 6 °C per minute until it reached 500 °C. The temperature was then kept constant at 500 °C for one hour and subsequently ramped up at a rate of 12 °C per minute until the final temperature of 1200 °C had been reached. After maintaining this temperature for three hours, heating ceased, and the chamber was allowed to cool down gradually. The following day we purged the deposition system with nitrogen to regain atmospheric pressure, and the coated samples were removed.

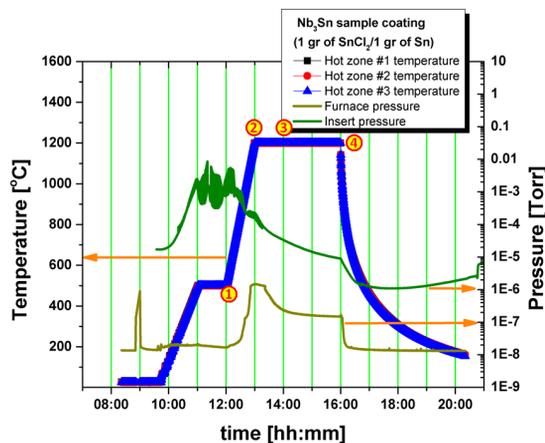


Figure 2: Heating profile used for sample coating. Temperature was measured in three different regions. Pressure conditions of furnace and insert are also shown.

LOCAL COMPOSITION

Local composition of the deposited coating was analyzed by energy dispersive x-ray spectrometry (EDS) with Hitachi 4700 field emission scanning electron microscope (FE-SEM). SEM provides an image of the coated surface and EDS gives elemental composition. SEM images of Nb₃Sn-coated surfaces have been previously presented with EDS results very close to the stoichiometric composition of Nb₃Sn [1, 2]. Similar structure was observed in our coating; a typical one is shown in Fig. 3. For the same coating parameters, we found similar grain structure in all the coated samples despite variation of substrate preparation.

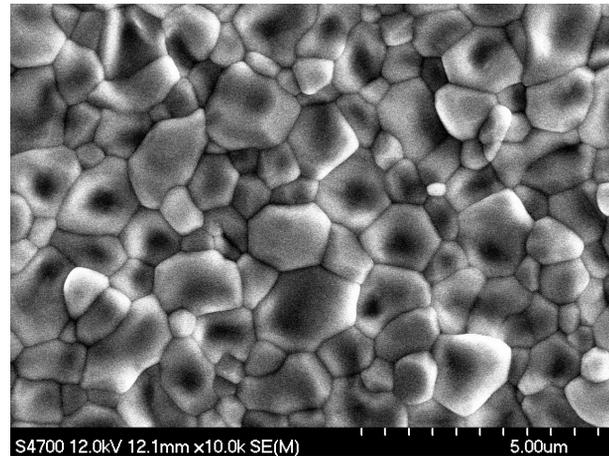


Figure 3: SEM image from a coated sample with substrate prepared with NP.

The electron beam in SEM/EDS spreads in three dimensions when it interacts with the sample to generate x-rays. The dimensions of electron interaction were approximated by [4],

$$z(\mu\text{m}) = \frac{0.1E_o^{1.5}}{\rho} \quad (1)$$

$$y(\mu\text{m}) = \frac{0.077E_o^{1.5}}{\rho}$$

where z is the depth of electron penetration, y is the width of the excited volume, $\rho = 8.92 \text{ g/cm}^3$ is the density of Nb₃Sn, and E_o is the accelerating voltage in keV. A theoretical expression for the range of an electron, the straight line distance between where an electron enters and its final resting place was also calculated individually for niobium and tin to avoid any ambiguity using [5]. It is found that the region from which the EDS information comes out is limited by escape of the produced x-rays. We also estimated the x-ray transmission fraction for Nb-L_α and Sn-L_α lines for different accelerating voltages. It is possible to increase the primary electron beam energy to penetrate the sample more deeply, but enough x-rays would not be coming out for analysis. It has been determined that EDS analysis with an accelerating voltage of 12-15 keV is best to analyze our coating because it results in the excited volume being within the range of our

grain size ($\approx 1 \mu\text{m}$) and thickness of coating ($\approx 1.5 \mu\text{m}$). Several measurements were done to determine the best data collection time for EDS. Instrumental statistical error was reduced by increasing data collection time, but the peak to background ratio fell. Analyzing the results, it was found that collecting data for 150-200s would be an acceptable compromise. Repeated measurements were performed in the same location with same instrumental parameters to estimate the range of instrumental reproducibility error, and found that the observed measurements always varies by 1-2 atomic percent.

Local composition of coatings was examined by EDS in several locations of each sample. Observed compositions were similar in each coated sample and were found to be independent of substrate preparation methods (BCP, EP or NP), and crystallinity (bicrystal or polycrystal) of the niobium substrate. Average tin content of 23.5 ± 2 atomic percent was observed in all the samples. The variation of compositions from position to position was consistent with reproducibility error, reflecting the composition uniformity. We found some carbon contamination and a small amount of Ti occasionally, but the ratio of Nb to Sn was not altered.

The possible artifacts that EDM, one of the available methods for cavity dissection, could have inflicted upon the coated surface were assessed before cutting a coated cavity. This was accomplished by cutting one of the coated sample into halves by EDM. Both halves were numbered before cut, and analyzed before and after cut by SEM/EDS. It was observed that the cutting process had developed cracks as far as $100 \mu\text{m}$ away from the cut edge. EDS revealed the presence Cu, Zn, Al, C and O up to this distance. It was likely that Al came from the stage used in EDM whereas Cu or Zn were derived from the brass electrode wire used during the cutting. C and O were absent before EDM cut, but appeared afterward and are believed to be handling contamination.

A milling process was employed instead of EDM to minimize all the possible artifacts. Temperature mapping of the cavity in operation was used to select locations for cutting samples. These were investigated by SEM/EDS. SEM images revealed the presence of unusual pits and cracks as shown in Fig. 4. Cracks in each sample found to have a preferential direction, and were intergranular. Cracks are suspected to be a consequence of the cutting process, but this is not confirmed. The average grain size in cavity samples was $\approx 2 \mu\text{m}$, larger than found in coupon samples. Observed pits are suspected to be responsible for poor cavity performance. EDS analysis performed in several areas showed a stoichiometry of 24.25 ± 2 atomic percent tin. We found O, C, Al and Cu contamination which were confirmed to be artifacts of the cutting process.

TOPOGRAPHY

The shallow penetration depth (approximately 100 nm) of RF into Nb_3Sn calls attention to the importance of surface topography. Explicit correlation between topography and performance has not been determined for Nb_3Sn yet, but it

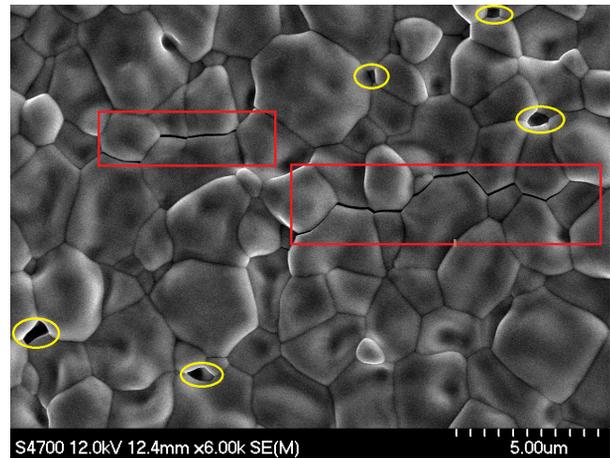


Figure 4: SEM image taken from a cut cavity sample. Cracks (marked with red rectangles) and pits (marked with yellow ovals) are visible.

has been shown to be important for niobium cavities [6]. The coating looked similar to the surface images presented by previous researchers. However, previous work on Nb_3Sn has not quantitatively characterized the coating's topography. A microscopic study is initiated to investigate the topography of Nb_3Sn coating in detail. The surface topographic measurement has been carried out with a Digital Instruments Nanoscope IV AFM in tapping mode using silicon tips with diameter $< 10 \text{ nm}$. Each sample were scanned in three different regions each with scan sizes $50 \mu\text{m} \times 50 \mu\text{m}$ and $5 \mu\text{m} \times 5 \mu\text{m}$. AFM images revealed dimples on Nb_3Sn grains formed by curved facets, Fig. 5. These dimples were also visible in SEM images as a dark spot in many grains, see Fig. 3.

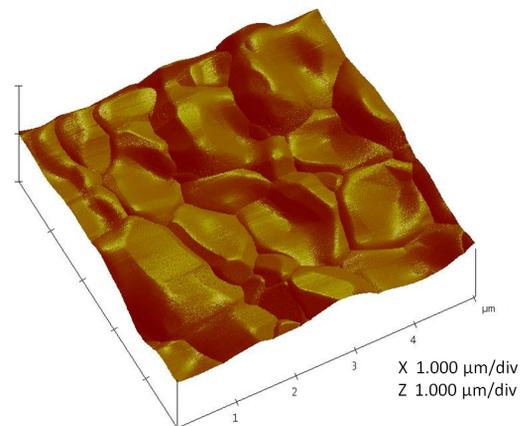


Figure 5: AFM image with scan size $5 \mu\text{m} \times 5 \mu\text{m}$ from coated sample with substrate prepared with NP.

The AFM data were collected as arrays of height values with 512×512 points and analyzed in terms of power spectral density (PSD) as before [7, 8]. The PSD is calculated by Fourier transform of the scan data to reveal the average contribution by features at different lateral scale. PSD was calculated for each of the 512 scans in each data set, and

averaged to obtain one dimensional average PSD. PSD profiles measured at different locations under the same scan condition were also averaged to get a representative PSD profile of each sample.

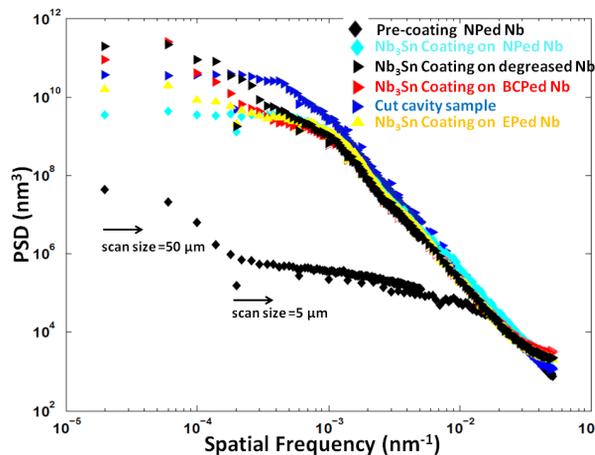


Figure 6: Average PSDs from Nb₃Sn coated surfaces with different starting conditions. Note the evolution of roughness compared to pre-coating nanopolished niobium surface.

Comparison of PSD results from Nb₃Sn coated surfaces and their pre-coating niobium surfaces shows that the coating process generates a characteristic topography which is independent of pre-coating topography (see Fig. 6). The nature of PSD profile from the Nb₃Sn coating was found very similar to PSD profile from niobium surface prepared with BCP [8], which is characterized by a straight line in high frequency region of the log-log plot. The average RMS roughness was found close to 70 nm in each coated sample for 5 μm × 5 μm. If the microscopic topography affects the cavity performance significantly, it will be a new challenge to overcome.

GENESIS OF COATING

Diffusion coating is the most promising method developed to pursue the best performing Nb₃Sn cavities. The coating procedures used by different research institutions are very similar, as most of them are based on the Wuppertal recipe. Coating structure and composition are determined by the process. Some fresh study was done to gain insight into the genesis of coating structure and composition. The coating process was stopped at different stages to examine the growth of Nb₃Sn coating. Nb samples prepared with NP or BCP were processed, and the coating process interrupted at point 1 - 4 shown in Fig. 2.

SEM images from different stages of the coating process are shown in Fig. 9. The formation of tin droplets on the niobium surface was noticed after one hour at 500 °C, which appear as bright circular features of variable sizes. The distribution of tin droplets appeared to be uniform with an average density of 0.3 droplets/μm². XPS survey scan was unable to detect any chlorine, shown in Fig. 7. Tin was detected by EDS only on bright features.

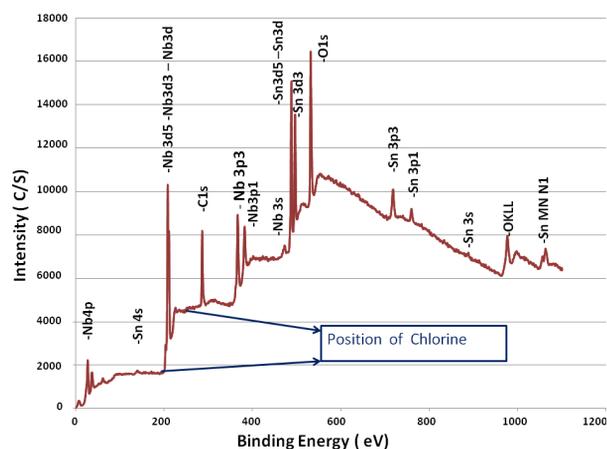


Figure 7: XPS data from a sample after one hour at 500 °C.

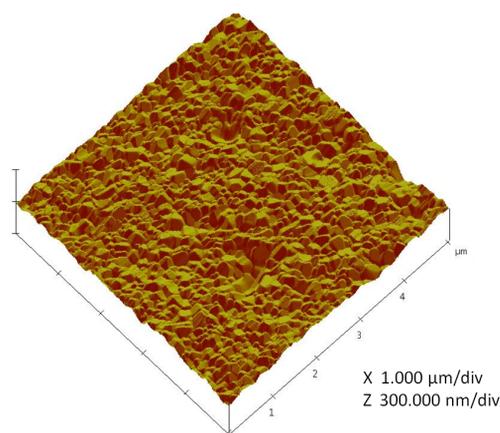


Figure 8: AFM image with scan size 5 μm × 5 μm from a sample after a minute at 1200 °C. Note the grain size and depressions on the surface.

A minute after reaching at 1200 °C, tin covered the whole niobium surface starting the formation of small grains. Some tin droplets were still visible. Considering only niobium and tin, XPS scan resulted ≈27 atomic percent of tin. SEM images showed depressions next to the nucleation sites, which was conformed with AFM images. An AFM image is shown in Fig. 8. EDS measured ≈20 atomic percent of tin in between these nucleation sites. EDS measurements of tin content from depressions next to the nucleation sites were only about ≈15 percent. Difference in XPS and EDS measurement suggests the formation of a thin layer with higher tin content on the niobium surface.

Complete coverage of the surface was noticed after an hour at 1200 °C. Grain sizes were noticed to be < 0.25 μm. EDS measured ≈21 percent atomic tin in most of the area. Some depressions, dark areas on the SEM image, were also observed in AFM images. The positions of these depressions seem similar to the positions of the tin droplets evident after one minute at 1200 °C, raising the question of causation. Completing the process, after three hours at 1200 °C, brings the grain size to about a micron size.

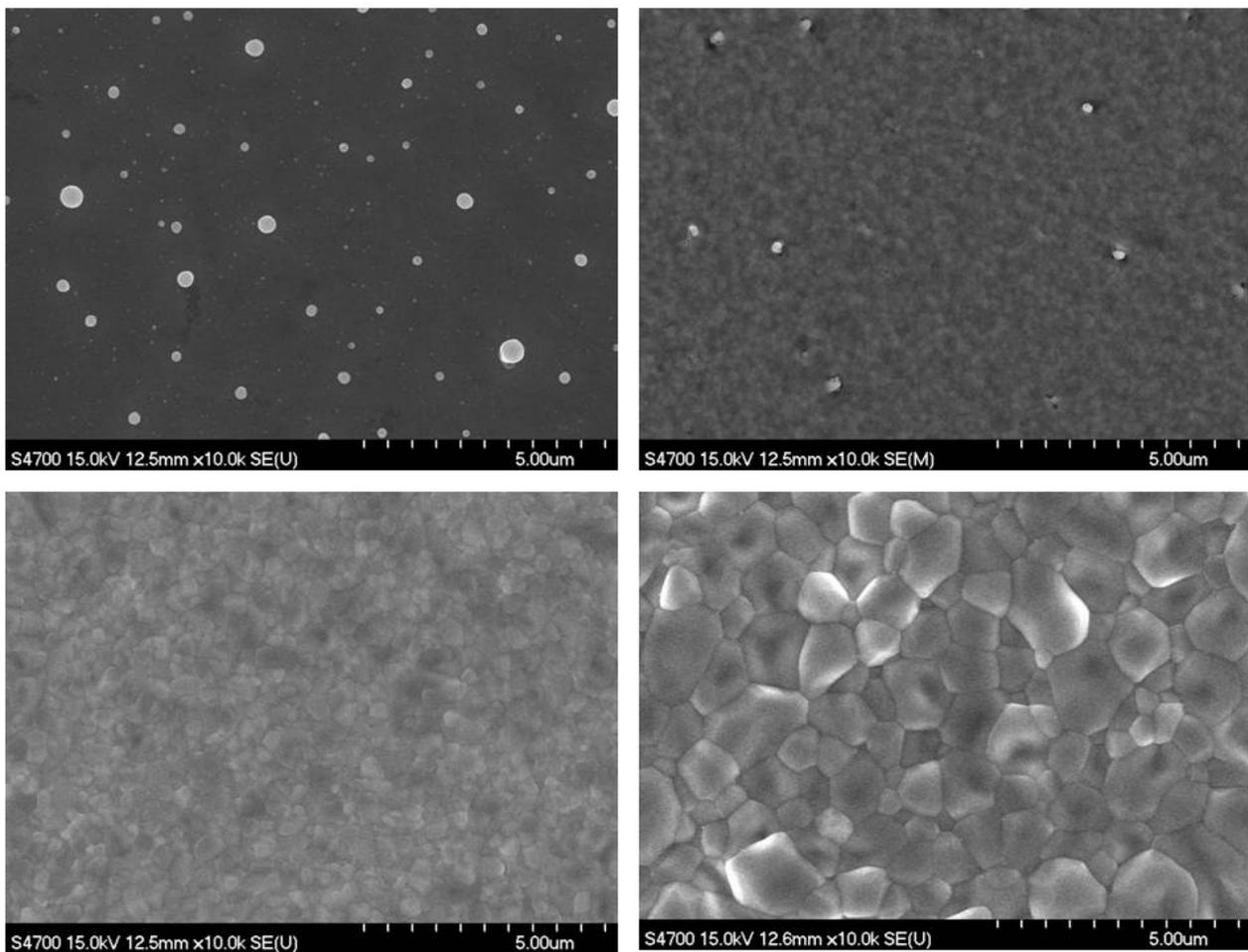


Figure 9: SEM images from samples prepared by interrupting the coating processes at points 1-4 (see Fig. 2) respectively. Figures on top are from NP samples and others are obtained from BCP samples.

SUMMARY AND FUTURE PLAN

Local composition and topography of Nb_3Sn coating prepared by the diffusion process were studied. Compositions were found not to vary with substrate preparation methods. The topography of Nb_3Sn coating deposited on niobium which had different preparation history was compared to their pre-coating topography. It is found that the coating process evolves a characteristic topography which is independent of pre-coating topography of the starting substrate. Results are discussed from experiments performed by stopping the coating process in different stages. Density of nucleation sites might play an important role to determine the resulting structure. It is planned to investigate the evolution of topography during the coating process.

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