CRYSTALLOGRAPHIC CHARACTERIZATION OF Nb₃Sn COATINGS AND N-DOPED NIOBIUM VIA EBSD AND SIMS *

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Abstract

Historically. niobium has been used as the superconducting material in SRF cavities. Due the high operational costs, other materials are currently being considered. Nb₃Sn coatings have been investigated over the past several decades, motivated by potentially higher operating temperatures. More recently niobium has been doped with nitrogen to improve the quality factor (Q) [1]. Currently, a need for better understanding still exists for both mechanisms. Electron backscatter diffraction (EBSD) has been shown to be a viable technique to determine the crystallographic orientation and the size of the NB₃Sn grains [2]. The EBSD maps obtained show a bimodal distribution of grain sizes with smaller Nb₃Sn grains found present near the Nb₃Sn/Nb interface. In addition to the Nb₃Sn coatings, N-doped niobium coupons were analyzed by EBSD and found that the coupon had preferred surface orientation. The EBSD analysis was found to be vital as specific grains could be targeted in secondary ion mass spectrometer (SIMS) to better understand the diffusion of nitrogen with respect to crystal orientation.

INTRODUCTION

Electron Backscatter Diffraction is a relatively new technique in the field of materials characterization. Even newer is its application in the field of superconducting radiofrequency (SRF) materials. This technique which utilizes both a scanning electron microscope and EBSD simultaneously, collects a micrograph and determines the crystal orientation of each pixel as the electron beam rasters across the sample's surface. This generates a colorized orientation image map (OIM) which details the surface orientation of each grain depicted in the image. Additional information can be generated such as grain size and grain misorientation.

Sample preparation governs the success of creating EBSD quality surfaces. Generally, vibratory polishing or other mechanical means of polishing are sufficient methods to provide these surfaces. However, niobium is noted to be especially difficult to generate EBSD quality surfaces by mechanical means. This makes other means of polishing necessary. One such preparation method is Focused Ion Beam (FIB) polishing. In addition to providing EBSD quality surfaces, FIB polishing provides unique control to prepare materials with egregious

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geometries and precise regions of interest. Additionally, FIB polishing is particularly useful when polishing materials which have varying degrees of hardness.

An experimental method for the sample preparation and EBSD collection of Nb_3Sn coatings on niobium substrates has been detailed by Tuggle et al. 2017 [2]. However, the FIB polishing technique can also be challenging. A major focus of this manuscript will be discussing some of the challenges which can make EBSD acquisition more successful, as well as outlining additional information gained as a result of EBSD analyses. Additionally, this document will address the application of using EBSD to assist in the characterization of N-doped niobium coupons.

PREPARATION OF NB₃SN SAMPLES

 10×10 mm polycrystalline fine grain niobium coupons were cut using an Electrical discharge machine (EDM) and buffer chemical polished (BCP) etched to prepare to prepare the sample surface. The niobium coupons were then coated with Nb3Sn utilizing a vapor deposition process at JLab. As the coating process varied as a part of other experiments, the details of the coating process can be found in U. Pudasaini et. al. 2019 [3].

NB3SN EXPERIMENTAL

To increase the efficiency of the FIB polish, the niobium substrates with a Nb₃Sn coating were mechanically prepolished at a 3° angle to remove as much bulk niobium as possible. The substrates were then mounted at 45° and loaded into a FEI NanoLab 600 Dual beam instrument to FIB polish as well as perform EBSD.

Primarily the sample is oriented such that the FIB beam is nearly parallel to the cross-section of the specimen (incidence angle <1°). During this step a protective coating of platinum is deposited on the surface of the Nb3Sn layer. Initially the FIB is set to the maximum accelerating voltage and current of 30 kV and 21 nA respectively, which allows for the quickest removal of material (Fig. 1a). It is during this step that most of the challenges present themselves. Due to the high energy of the beam, cascading becomes evident (Fig. 1b.). The platinum coating prevents most of the cascading therefore it is crucial to deposit a thick platinum layer. Insufficient platinum will sputter away quicker at the material edge potentially exposing the sample surface to the FIB beam. It was found the platinum coatings thicker than 3µm were enough protection for the underlying Nb3Sn coating. During the initial removal step using a voltage of 30 kV, some beam damage was unavoidable, and cascading was obvious. It was found that

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Figure 1: The above images outline the process to collect quality EBSD OIM maps. a.) Initial material removal at the highest beam conditions of 30 kV/21 nA led to b.) surface artifacts and cascading. c.) Performing a cleaning crosssection with the same beam conditions adjacent to the working surface removed the cascading artifacts. d. Subsequently the sample was rotated so that incident beam was paralell to the working surface and with the conditions lowered to 5 kV/1.3 nA and then finally to 2 kV/0.71 nA. \therefore e.) The result was a quality surface viable for EBSD.

R the cascading could be mitigated by performing a cleaning cross-section at 30 kV adjacent to the FIB cut. This step was repeated until the cascading was removed (Fig. 1c.)

Once the cascading was removed, the sample was rotated so that the electron beam was perpendicular to the sample surface (incidence angle $\approx 90^{\circ}$). The previous step of 30kV causes a damage layer of approximately 5-10 nm. ^O Furthermore, the fast removal of material causes sputtered niobium to be redeposited on the sample surface. This must be removed prior to the acquisition of EBSD OIM maps. The FIB conditions were lowered to 5 kV/1.3 nA. The raster window was reduced to scan only across the area of interest for EBSD, typically the Nb₃Sn layer and a small portion of the niobium substrate. As the Nb₃Sn layer thickness dictates the time needed to remove the damage layer, there is no set time for this step. However, having the correct elapsed time for the FIB beam exposure during this step was critical for acquiring quality EBSD maps. Too little time would not allow for the Nb₃Sn grains to index well. Too much time would cause the Nb₃Sn to sputter faster than the niobium substrate which causes the interface to index poorly (Fig. 2). It is suggested that during this step EBSD test scans are performed intermittently to determine if the Nb₃Sn layer has begun to index.

Following the 5 kV/1.3 nA polish, the layer was further polished with 2 kV/0.71 nA FIB conditions. This reduced



Figure 2: a.) An SEM micrograph showing a sample which had been over polished. A topographical difference is observed at the Nb3Sn/niobium interface. b.) As a result, the EBSD OIM shows poor indexing along the interface as well as some grain boundaries.

the damage layer thickness and increased the indexing quality of OIM. As before, there is not a set time for the FIB to polish during this step. However, it was found that using 50% more time than the 5 kV/1.3 nA polish generally removed enough of the damage layer for the Nb3Sn grains to index well.

The purpose to collecting EBSD OIM maps was to identify details which help to understand the nucleation and growth of the Nb₃Sn on a niobium substrate. Many samples were analyzed; however, certain attributes were consistent between samples. At the Nb₃Sn/niobium interface, small grains were observed to be present. Increasing the coating thickness via overcoating, (repeated cycles of Sn vapor deposition), did not change the presence of the small grains at the interface (Fig. 3). Instead, the bimodal distribution of small and large grains became more evident.

The presence prompted the question of whether the concentration of tin changed as a function of proximity to the interface. A portion of the cross-section was extracted via a FIB liftout and analyzed in a JEOL JEM 2100 TEM equipped with an integrated EDS system. The analysis was performed using an accelerating voltage of 200kV and a beam current of 107 µA. Several EDS spot analyses were performed in a path approaching the Nb₃Sn/niobium interface from the Nb₃Sn layer (Fig. 4). It was observed that in the bulk of the Nb₃Sn layer, the concentration of tin was approximately 20 at.% Sn. In the smallest grain near the interface the concentration of tin was found to be 10 at.% Sn. This suggests that the Nb₃Sn grains are nucleating at the interface as the tin concentration approaches a critical concentration. For detailed information regarding the nucleation and growth of Nb₃Sn please see Pudasaini et al. 2019.

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Figure 3: EBSD OIM maps of Nb₃Sn overcoat samples which the total elapsed deposition was a.) 2 hours b.) 6 hours and c.) 78 hours. The change in coating time did not affect the presence of small grains at the interface. Reproduced with permission from Tuggle et al. 2019 [4].



Figure 4: TEM images of a FIB liftout of a Nb₃Sn coated sample. a.) Shows the overall sample. b.) Illustrates locations in which EDS analyses were performed. c.) Shows a small grain on the Nb₃Sn/Nb interface. d. Plot showing how the concentration of Sn changes near the interface.

N-DOPED NIOBIUM

Presently, the determination of nitrogen concentration as a function of grain orientation is highly motivated. Previous

and] experiments have shown that grain orientation can play a publisher, role in nitride formation on the surface which may subsequently affect the diffusion of nitrogen within the grains [5]. EBSD was performed to generate OIM maps to locate differing grains within a sample. Subsequent SIMS work, analysis was performed on specific grains to quantify carbon, oxygen, and nitrogen concentrations as it pertains he to a specific orientation. author(s), title of

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Specifically, for the SIMS analysis, a sample denoted as NL 115 was analyzed. This specimen was pre-annealed at 900°C and EDM cut to form 6 ×10 mm coupons. The sample was BCP etched to remove 50 µm of material followed by "nanopolishing" and electropolishing (EP) to the remove an additional 25 µm. The coupon was then heated attribution to to 800 °C where it was exposed to a flow of nitrogen for 3 minutes followed by a 60 minute vacuum anneal. Prior to the characterization by EBSD and SIMS, the sample underwent additional surface treatments which are detailed in Spradlin et al. 2019 [6]. A final EP step was performed maintain to remove an additional 5 µm to remove surface nitrides.

EBSD was once again performed in the FEI NanoLab 600 Dual beam instrument equipped with an EDAX TSL $\frac{1}{2}$ EBSD camera. The samples were then mounted at 45° to ease the transition between FIB and EBSD usage. The FIB was used to mark an area adjacent to the testing area to this ensure the correct locations would be found in the bution of following SIMS analysis. The EBSD was performed with a 70° tilt (20° incident beam) utilizing an electron beam with 30 kV/21 nA accelerating voltage and current. · distri Multiple overlapping orientation image maps (OIM) were acquired so that the OIM maps could be stitched post processing. The electropolished samples were noted to $\overline{\xi}$ provide superb sample finishes, rendering data cleaning unnecessary. It was found that the samples had a preferred 201 surface orientation of either the near [111] or near [001] 0 crystal orientations (Fig. 5). Although the surface 3.0 licence (orientation was preferred, some stray opposing [111] or [001] grains were observed to be present in both preferred orientations. Near [010] grains were not observed in the under the terms of the CC BY OIM.



Figure 5: EBSD OIM maps of two different N-Doped samples. a.) Sample which has a preferred orientation of [001] surface grains as observed by the red colored grains b.) Sample which has a preferred orientation of [111] surface grains as observed by the blue colored grains.

from this Following EBSD, the NL 115 coupon was loaded into a Cameca SIMS 7fGEO, to determine the concentration of carbon, oxygen, and nitrogen as a result of dependence of grain orientation. A Cs+ primary ion beam was rastered

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and over targeted grains with an area of 150 µm2 utilizing a ler. 63 µm2 analysis area. An impact energy of 8 kV was used (5 kV source/-3 V sample) with a current of 100 nA. 12C, 16O, 93Nb14N negative secondary ions were detected in addition to a 93Nb reference signal. Specific grain work. orientations were targeted which include near [111] (blue) and near [001] (red). Additionally, carbon and nitrogen þ concentrations within a single grain were evaluated. Fig. 6 Ē provides an OIM with SIMS locations noted. Additionally, Fig. 6 provides the SIMS analysis which correspond to the locations noted on the EBSD map.

author(s). Quantification was made possible by monitoring the ${}^{12}C$, ¹⁶O, ⁹³Nb¹⁴N signals from ion implantation standards. The the provided implant standards contained ¹²C to a dose of 1×10^{15} atoms/cm² at 160 keV ¹⁶O, to a dose of 2 attribution 2×10^{15} atoms/cm² at 180 keV and ¹⁴N to a dose of 1×10^{15} atoms/cm² at 160 keV. Four locations were tested on the implant standard/day and an average relative sensitivity factor (RSF) was determined for each ion. The maintain average RSF was applied to the ¹²C, ¹⁶O, ⁹³Nb¹⁴N signals of sample NL 115 to calculate the atomic ppm (ppma) of each ion.



0 Figure 6: a.) EBSD OIM map of the NL 115 N-Doped licence sample. This sample had a near [001] (red) preferred surface orientation with a rare [111] (blue) grains present. Both [001] and [111] grains were targeted for SIMS analyses with the locations marked on the image b.) Carbon, oxygen and nitrogen concentrations as a function 00 of sputtering depth are depicted.

The SIMS analysis showed differences in the carbon, oxygen and nitrogen concentrations as a function of surface grain orientation. The carbon and oxygen signal was noted to diffuse up to 0.5 µm for the [111] grains before reaching a baseline signal. The [001] carbon and oxygen signal was observed to taper much quicker, reaching the baseline signal around 100 nm. It was observed that the baseline signal for carbon, oxygen and nitrogen all differed with the concentrations from the [111] grains appearing to be less. Additionally, the sputter rate ay was determined to be faster for the [111] grains compared to the [001] grains. Table 1 summarizes the results. As the structure is cubic and the sample underwent a 60 min annealing step at 800°C, this result is unexpected. The cause of these concentration differences is currently being investigated.

Table 1: Summary of SIMS Analysis	
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Spot	Carbon Content ¹ (ppma)	Oxygen Content ¹ (ppma)	Nitrogen Content ¹ (ppma)	Sputter Rate (nm/s)		
Near [001] Grains						
1	44.9	59.6	585	2		
2	47.7	64.9	454	1.080		
3	24.4	63.8	484	1.038		
4	35.2	55.8	524	1.016		
5	35.5	57.4	515	1.156		
6	35.1	56.7	502	1.119		
Near [111] Grains						
1	17.4	29.8	216	1.341		
2	22.2	37.5	325	1.130		
3	18.8	27.4	256	2.221		

¹ Baseline concentration taken at a depth of 0.6µm

² Raster reduction performed, crater depth not measured

SUMMARY

Having an exceptionally smooth surface is crucial to the success of acquiring meaningful EBSD OIM maps. The surface must not only be smooth, it must also have a minimal damage from the ion beam. FIB polishing is a useful technique to remove the damage layer. This manuscript identified common challenges to overcome such as removing artifacts, notably cascading and redeposition. Additionally, over-polishing was explained to cause topographical differences making indexing difficult at the interface of Nb₃Sn.

As small grains were evident at the Nb₃Sn/niobium interface, well prepared samples were crucial to determine the grain sizes of these smaller grains. These smaller grains were found to be present without regard to the exposure time of Sn vapor deposition. The observation of these smaller grains warranted TEM-EDS analysis, which showed that the concentration of tin was notable less at the interface as opposed to the bulk regions of the Nb₃Sn layer. The tin concentration was found to be as low at 10% in a small grain adjacent to the interface.

EBSD was additionally performed on a N-doped niobium sample. This technique proved to be useful in identifying that the N-doped samples had a preferred surface orientation to either [111] or [001] surface planes. The orientation, albeit preferred, was not pure. This allowed for near [001] and [111] grains to be located by EBSD and individually analyzed by SIMS. The carbon and nitrogen concentrations were observed to differ between the [001] and [111] grains. As niobium is a BCC crystal structure, the diffusion of carbon and nitrogen should not be dependent on grain orientation [7]. Rather it is more likely that the RSF is grain orientation dependent which caused the difference to be observed in the concentration. Refinement of characterization calibration will continue.

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