

POST-PROCESSING OF Nb₃Sn COATED NIOBIUM*

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Abstract

Practical SRF cavities may be subjected to one or more processes after nominally complete preparation. Successful implementation of such processes in Nb₃Sn coated cavities requires the understanding of material's response to these treatments. SRF-grade Nb samples, coated with Nb₃Sn by the widely used tin vapor diffusion process were subjected to one or more of the following: hydrofluoric acid (HF) rinsing, oxypolishing, buffered chemical polishing (BCP) or electrochemical treatment. They were examined by materials characterization techniques including scanning electron microscopy (SEM) with energy dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The effects compared to niobium are different enough in most cases that further development is desirable to routinely obtain a favorable result.

INTRODUCTION

Continued R&D efforts are bringing niobium SRF cavity performance close to the maximum possible limit, pushing researchers to explore alternate materials for better performance and cost reduction. Because both the critical temperature and superheating field of Nb₃Sn are nearly twice that of niobium [1], it promises higher operating temperature and accelerating gradient, resulting in significant cost reduction of SRF accelerators. Despite the brittleness and lower thermal conductivity of bulk Nb₃Sn, Nb₃Sn-coated SRF cavities are now produced routinely by depositing few micron thick Nb₃Sn layer inside of Nb cavities using the tin vapor diffusion technique [2-4]. Several post-processing techniques (EP, BCP, annealing, impurity doping etc.) have been developed for niobium cavities to enhance the cavity performance, but similar techniques are not yet researched in depth for Nb₃Sn. The controlled removal of top few layers of coated surface may reduce surface defects and contamination by exposing a good quality Nb₃Sn underneath. Development of such techniques can provide control over topography of Nb₃Sn coated surfaces, which appear to have roughness that could negatively impact the cavity performance. Nb₃Sn, an intermetallic compound, could pose unique challenges to apply material removal or polishing techniques available because only few microns thick material is present to process. Aiming towards a suitable material removal technique for Nb₃Sn, different techniques (HF rinsing, oxypolishing, BCP and EP) were attempted on Nb₃Sn coated SRF-grade niobium samples. Details on coating process can be found in [5]. Nb₃Sn coated sam-

ples used in this work were prepared in different runs during the course of material studies, and may or may not represent the identical coating conditions. In this contribution, response of Nb₃Sn coated surface to different removal techniques is presented.

HF RINSING

XPS analysis of Nb₃Sn coated samples shows that the surface is covered with Nb₂O₅ and SnO₂ [2, 6]. It is known that the application of HF rinse dissolves Nb₂O₅, and is expected to remove SnO₂. Four samples coated with Nb₃Sn were immersed in bottle-strength, 49% HF solution for 1, 5, 30, or 60 minutes at room temperature. Samples were then removed and rinsed with de-ionized water. SEM examination of samples rinsed for 1 and 5 minutes did not show any significant changes on microstructure. However, new features emerged after prolonged HF dipping for 30 or 60 minutes. Comparison of AFM images before and after 30 minutes HF rinse are shown in Figure 1.

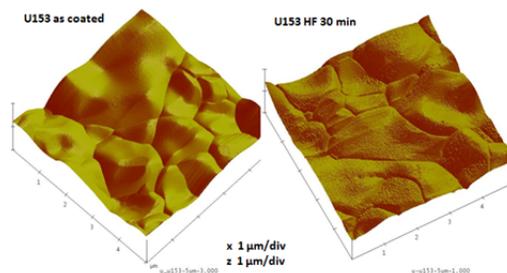


Figure 1: AFM images of Nb₃Sn coated sample U153 before (left) and after (right) 30 minutes HF rinse. Note the new features that emerged after HF rinse. The change in the appearance of grain boundaries is evident.

Grain facets appeared sharper after 60 minutes of HF rinsing indicating a gradual etching of the coated surface. SEM images are shown in Figure 2. It also shows the sharpening of grain boundaries, which was confirmed with AFM.

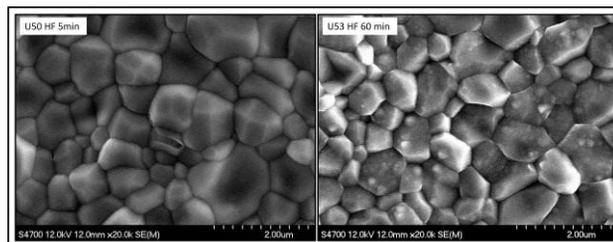


Figure 2: SEM images from sample after 5min and 1 hour HF rinsing.

EDS did not show any significant differences in the composition following HF rinsing for any duration. Note that the depth resolution of EDS measurement may not be enough sensitive to evaluate the change in composition at

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the surface. XPS surface analysis showed Nb to Sn ratios of 3.46, 2.98, 3.59 and 3.60 for 1, 5, 30 and 60 minute rinsed sample respectively. Note that XPS measurements for non-rinsed Nb₃Sn coated samples typically show these ratios less than 3.

OXYPOLISHING

XPS analysis of Nb₃Sn coated samples shows that the surface is covered with oxypolishing is one of the processes that has been applied to Nb₃Sn coated cavities [7-10]. Here, an oxide layer is grown on the Nb₃Sn coated surface via electrochemical anodization, and subsequently rinsed with HF to remove the oxide layer. It can take multiple cycles of anodization and HF rinsing to achieve the desired amount of material removal. The thickness of the oxide layer can be controlled by applying a fixed voltage. A fixed cell voltage of 10, 20, 30, 40 or 50 V was applied to grow anodic oxide layers on Nb₃Sn coated samples using 15% NH₄OH solution as an electrolyte. The corresponding oxide layer thickness was then determined by XPS sputtering profiles, calibrated by FIB cross-section combined with SEM [11]. It was found that ~ 2.4 nm/V of an oxide layer was grown on the surface, see Figure 3. This thickness-voltage relation is close to Stimmell's observation, 2.8 nm/V [12].

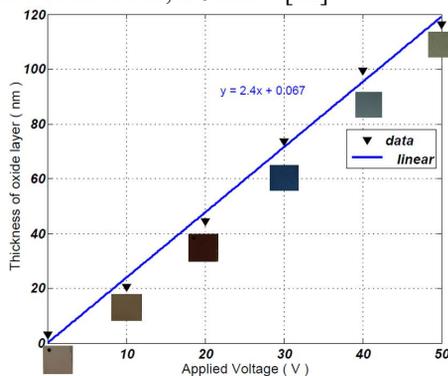


Figure 3: Thickness-voltage relation for oxide layer grown in Nb₃Sn. The change in color of each sample corresponding to anodization voltage is shown in the square image below each data point.

Each anodized sample was then given an HF rinse for 10 minutes. After few seconds of exposure to HF, the color of each sample changed to grey, typical appearance of Nb₃Sn coating. SEM examination of each sample revealed new features on the surface, similar but smaller than the features developed after one hour of HF rinse, see Figure 2. An example of such surface is shown in Figure 4. It is speculated that the evolution of new features was due to the longer exposure to HF. Three Nb₃Sn coated samples were then anodized for 30 V each, and HF rinsed for 1, 2, or 5 minutes. Sample rinsed for 5 minutes showed more residue than the sample rinsed for 1 or 2 minutes, as shown in Figure 4. AFM examination of sample that was rinsed for 2 minutes showed some residues that did not appear in SEM image. Residue formation on an oxypolished Nb₃Sn surface had also been reported recently [12].

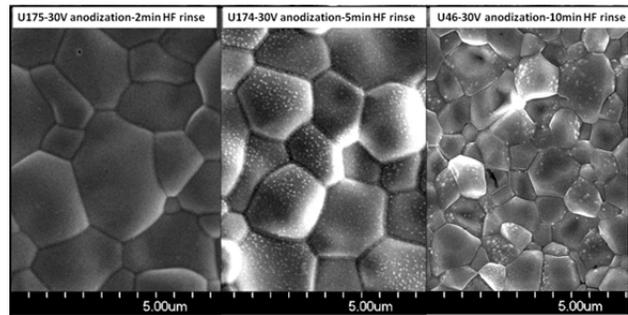


Figure 4: Surfaces obtained by HF rinsing of 30 V anodized samples for different interval. Note that new features were developed after 5 minutes.

In another set of experiments, 4 samples coated with Nb₃Sn were subjected to 1, 2, 3 and 4 cycles of 50 V anodization followed by 90 s HF rinsing. Using thickness-voltage relation, it is expected to grow and remove 120, 240, 360 and 480 nm thick oxide layer. Each sample shows some residue on the surface following the treatment, as shown in AFM image, Figure 5. Two niobium samples (100 μm BCP and 800 °C x 3 hours annealed) were given 3 and 4 cycles of similar oxypolishing. Similar residues appeared on the surfaces following the treatment suggesting that the features seen after oxypolishing of Nb₃Sn might not be a unique observation for Nb₃Sn. Further analysis is underway. No surface degradation by hole formation was seen that had been reported in the past for removal corresponding to total voltage of ~200 V [13]. EDS analysis of oxypolished samples shows the usual composition where as XPS analysis showed Nb to Sn ratios to of 3.22, 3.70, 3.30 and 3.56 for oxypolished samples for 1 to 4 cycles respectively.

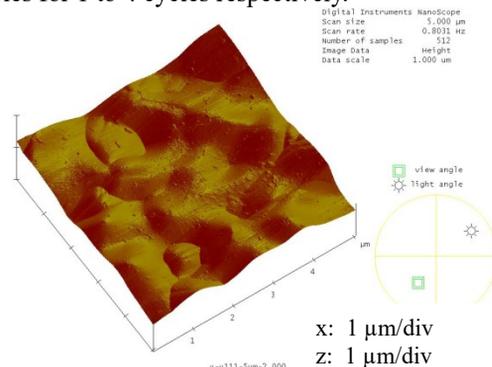


Figure 5: AFM image from sample U111, that received 4 cycles of 50V anodization followed by 90 s HF rinse. Note the small features on the surface.

BCP

Standard BCP solution, a mixture of 49% HF, 70% HNO₃ and 85% H₃PO₄ by volume ratio of 1:1:1 or 1:1:2 was applied to Nb₃Sn coated samples. The treatment was done for 5 seconds at 17 °C, which corresponds to niobium removal rate of ~8 or 3 μm/min for 1:1:1 or 1:1:2 BCP solution respectively [14]. The resulting surfaces from 5 seconds flash BCP experiments are shown in Figure 6. Note that, the sample U128 was given extra HF rinse for 30 minute after 1:1:2 BCP as it appeared dark brownish after the treatment. However, HF rinse did not

change the visual appearance. Some grains in U128 showed HF rinsed features, pointed by an arrow in Figure 6, which appeared similar to Figure 1. It is evident that BCP solution rapidly attacks Nb_3Sn surface by faceting grains resulting in a very rough surface. Combination of 1:1:2 and 1:1:1 BCP treated surface shows the evolution of surface compared to as coated Nb_3Sn surface, shown in Figure 6. Note that the EDS measurement shows similar composition prior the treatment. XPS ratios of Nb to Sn were found to be 3.08 and 3.52 for U128 and U162.

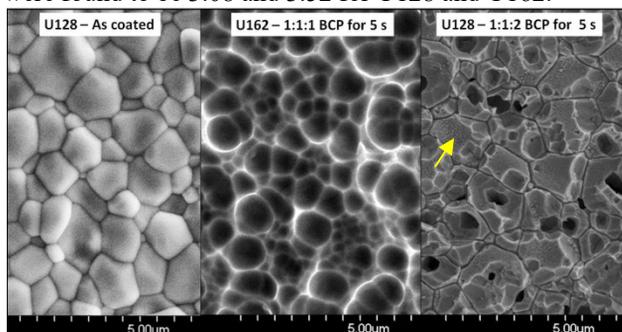


Figure 6: SEM images of Nb_3Sn coated samples before and after flash BCP for 5 seconds. Note that darker areas represent the concave structures in sample U162, which were confirmed with AFM. Bright curves are sharp edges.

1:1:1 BCP was done for 16, 32s, or 50 seconds on Nb_3Sn coated samples to observe the renormalization of substrate for future coating. Evolution of surface is shown in Figure 7. It indicates that a minimum of 10 μm BCP is needed to renormalize the substrate niobium.

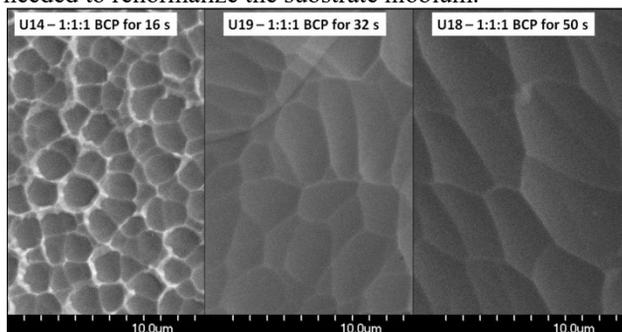


Figure 7: Evolution of Nb_3Sn coated Nb following BCP.

ELECTROCHEMICAL TREATMENT

Electropolishing (EP) is another successful technique used on niobium cavities for material removal as well as smoothing of the surface. Typical EP consists of 1:9:1:10 volume ratio of the mixture of 49% HF and 95-98% H_2SO_4 with current density 30-100 mA/cm^2 [14]. Nb_3Sn coated samples were introduced first in a standard 1:10 EP solution at room temperature for 15 and 30 minutes. SEM examination of samples following the process shows no obvious change in the surface indicating the stability of Nb_3Sn in EP solution. Attempts were made to determine the current-voltage (I-V) characteristics for electropolishing of Nb_3Sn at 6°C and 20 °C, but all the Nb_3Sn material was removed from the surface before reaching the end of the intended I-V curve. An exploratory electrochemical treatment was given to a sample in a standard EP solution with cell voltage of 8.5

V (current density $\sim 70 \text{ mA}/\text{cm}^2$) at 6 °C for one minute, similar to the one that is used for niobium sample polishing. Since EP is fairly a new approach for Nb_3Sn , the mechanism of material removal is not known. This experiment was expected to provide some clues for further investigation. AFM image of obtained surface is shown in Figure 8. Surprisingly, the surface appeared smoother compared to other untreated sample. Etching pits that were obtained with flash BCP were absent in resulting surface. EDS examination did not find any difference in composition following the treatment. The ratio of Nb to Sn was found to be 2.95, similar to the sample dipped in EP solution.

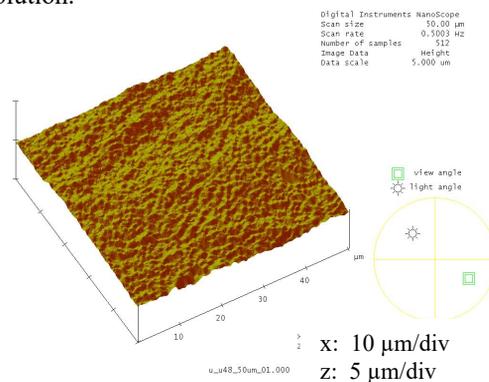


Figure 8: Sample U48 after electrochemical treatment for 1 minute with 8.5 V DC voltage at 6 °C.

SUMMARY AND FUTURE WORKS

We applied various post-processing techniques available for niobium to Nb_3Sn coated samples. It is clear that HF gradually etches the Nb_3Sn surface. The genesis of new features developed after prolonged HF rinsing of anodized/ non- anodized samples is not understood yet. It could be a result of different removal rate for niobium and tin or the precipitation of reaction products. Scanning auger microscopy (SAM) will be used to probe these features in detail. XPS yielded values of Nb/Sn were found to increase slightly following each treatment. It is possible that as coated sample may contain tin rich layer on the surface, resulting in lower Nb/Sn ratios. BCP treatment to Nb_3Sn appears to attack the surface rapidly producing a very rough surface by forming depressions with sharp edges. Examined surfaces obtained by longer BCP suggested a minimal removal of 10 μm to renormalize the niobium surface by removing residual topographical features. Preliminary electrochemical treatments are encouraging to further investigation. An effort is underway right now to study mass transfer characteristics for Nb_3Sn EP.

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