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EFFECT OF DEPOSITION TEMPERATURE AND DURATION ON Nb_3Sn DIFFUSION COATING*

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Abstract

Nb_3Sn is a potential candidate to replace Nb in SRF accelerator cavities to reduce cost and advance performance. Tin vapor diffusion is the preferred technique to realize such cavities by growing a few microns thick Nb_3Sn coating on the interior surface of the niobium cavity. The coating process typically uses temperatures of 1100–1200 °C for 3–6 hours. It is important to better understand the coating process, and optimize the coating parameters to overcome the current limitation on the performance of Nb_3Sn coated SRF cavities. We investigate Nb_3Sn coatings prepared in the temperature range of 900–1200 °C and duration of 3 - 12 hours using various material characterization tools. Variation of these parameters appears to have notable effect on microstructure and topography of the obtained surface.

INTRODUCTION

The critical temperature and superheating field of Nb_3Sn are nearly twice that of niobium [1]. Successful fabrication and application of Nb_3Sn made cavities could allow more efficient accelerator operation at higher temperature (e.g. at 4.2 K instead of 2 K) resulting in significant cost reduction of SRF accelerators. The brittleness and lower thermal conductivity precludes SRF cavity fabrication from bulk Nb_3Sn, but thin films have been realized by depositing few micron thick Nb_3Sn layer inside of Nb cavities by tin vapor diffusion [2–7]. The main aspect of this technique is to create tin vapor, and transport it to niobium substrate at temperature >930 °C, determined by binary phase diagram to form Nb_3Sn exclusively [8]. A small amount of tin chloride, which evaporates at ~ 500 °C and forms particles and thin film of tin on niobium is also included during the process to enhance Nb-Sn nucleation [9]. So, a typical tin vapor diffusion technique for Nb_3Sn features two steps – nucleation at 500 °C for 1 - 5 hrs and deposition at 1100–1200 °C for 3 –6 hours. Figure 1 illustrates the coating process at Jefferson Lab, which features one-hour nucleation step at 500 °C followed by a 3–6 hrs coating step at 1200 °C [10]. It is important to understand the effect of these parameters on the resulting Nb_3Sn coatings to optimize the process, and to overcome the current limitations on the performance of Nb_3Sn coated SRF cavities.

We investigated Nb_3Sn coatings prepared at the temperature range of 900–1200 °C and durations of up to12 hours using various material characterization tools. First results are reported in this contribution.

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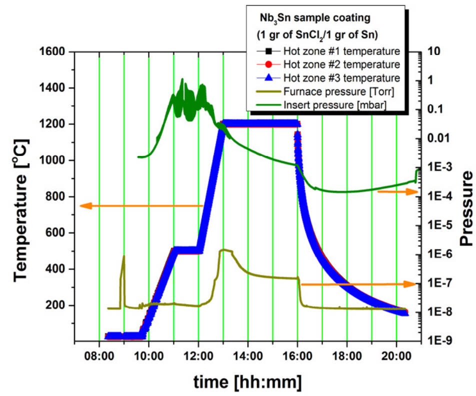

Figure 1: A typical Nb_3Sn sample coating process at Jefferson Lab.

EXPERIMENTAL

The niobium samples were 10mm × 10 mm coupons, cut by EDM from 3 or 4 mm thick, high RRR (~300) sheet material of the type used to fabricate SRF cavities. All samples were subjected to buffered chemical polishing etch (BCP) with minimum removal of 50 µm. A subset of those samples further received metallographic polishing, also known as nanopolishing (NP), suitable to obtaining smoother substrate surfaces for topography studies. The average roughness of NP samples was below 5 nm which was measured from 50 µm × 50 µm scan areas using atomic force microscopy (AFM). Another subset of samples was electrochemically anodized in 15% NH_4OH solution by applying a fixed cell voltage of 30 V. Thickness of the oxide layer was estimated to be ~80 nm for those samples using the thickness-voltage ratio from [11].

Niobium samples were then coated with Nb_3Sn under varying deposition parameters. The deposition temperature and duration are shown in Table 1. The nucleation step was fixed as usual, and identical experimental setups were used for each experiment. The temperatures were measured with thermocouples attached to the sample chamber. The duration of deposition was accounted right after the sample chamber reach the target deposition temperature. A fixed amount of $SnCl_2$ (0.5 g) and Sn (1.4 g) was supplied for each experiment at the beginning. Tin was loaded in the same crucible made of niobium, whereas $SnCl_2$ was packaged in Nb foil.

Table 1: Investigated temperatures and durations of Nb_3Sn diffusion coating.

Temperature (°C)	900	1000	1100	1200
Duration (hr)	3, 12	3, 12	3, 12	0.1, 3, 6

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Elemental composition and microstructure were examined with a Hitachi 4700 field emission scanning electron microscope (FE-SEM) equipped with an energy dispersive X-ray spectroscopy (EDS) detector with 12 or 15 kV electron beam. Topographic examination was carried out with a Digital Instruments IV AFM in tapping mode. Five different areas from each sample were scanned at 50 µm × 50 µm and 10 µm × 10 µm with point resolution of 512 × 512. Coating thickness was determined with XPS sputter profiling. Sputtering was accomplished via an argon ion source at 5 kV over a 2 mm × 2 mm area. XPS depth profile data was collected at 50 W/15 kV with a spot size of 200 µm, 45° take off angle and 280 eV pass energy with a PHI Quantera SXM.

RESULTS AND DISCUSSION

Coating experiments at 900 °C consumed a very small amount of tin (<10 mg), leaving most of tin in the crucible. Coatings obtained after 12 hours on NP and BCP samples were very similar with thread-like structures and very few pronounced grain boundaries (not visible in the image) on the surface. Pre-anodized samples on the other hand shows the well-connected usual Nb_3Sn structure as shown in Figure 2. EDS analysis showed 16 ± 1 at. % tin in each sample with. A similar result was obtained for 3 hours of deposition at 1000 °C, except the BCP sample lacked thread-like structure compared to the NP sample, and shows usual grains. EDS shows 21±1 at% tin. Depressions were noticed in the grains.

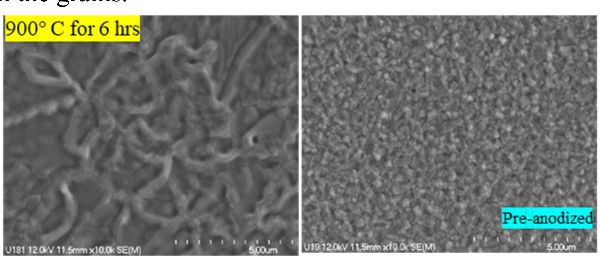

Figure 2: SEM images from pre-anodized [right] and regular BCP sample coated at 900 °C for 12 hours [left].

SEM images in Figure 3 compare the structure and topography of coatings prepared at 1000–1100 °C. Obtained coating after 12 hours of deposition at 1000 °C matches the usual appearance of Nb_3Sn. NP samples showed some abnormal grains, potential patchy areas of 20–40 µm in size and voids, but such structures were absent in case of pre-anodized and regular BCP samples. Patches showed 1–2 at. % less tin than usual Nb_3Sn composition of 24±0.5 at. % Sn from adjacent areas. Note that such patchy regions, cited before are large areas of single crystal Nb_3Sn, which are relatively thinner [12–14]. AFM images, not shown here showed some potential tin residue at the surface. In some cases, patchy areas appeared to have relatively more residue compared to areas with regular grains. Similar coatings were obtained with deposition temperature of 1100 °C for only 3 hours, but with a smaller grain size. The NP sample still showed some patch-like structures, but less frequently compared to similar samples coated at 1000 °C. A significant increase in grain sizes was noticed following the extended deposition duration of 12 hours at 1100 °C. No patches were seen in this case. EDS analysis shows usual Nb_3Sn composition. A few voids were present in some areas.

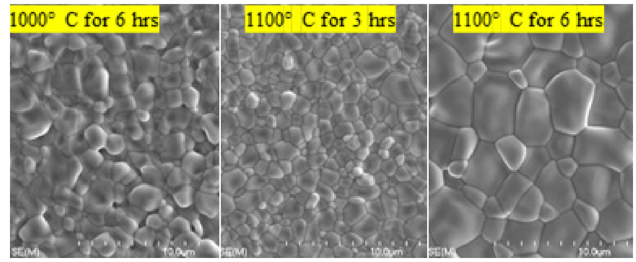

Figure 3: Microstructure of Nb_3Sn prepared at 1000–1100 °C for different durations on NP samples.

Short deposition for five minutes at 1200 °C resulted in some patchy regions in NP sample once again. Occurrences of such areas were less prominent in BCP treated pre-anodized and regular samples. Note that no tin chloride was included in this experiment. The coating produced after three hours of deposition at similar conditions resulted in larger grain size. The grain size further increased with longer coating of 6 hours as shown in Figure 4.

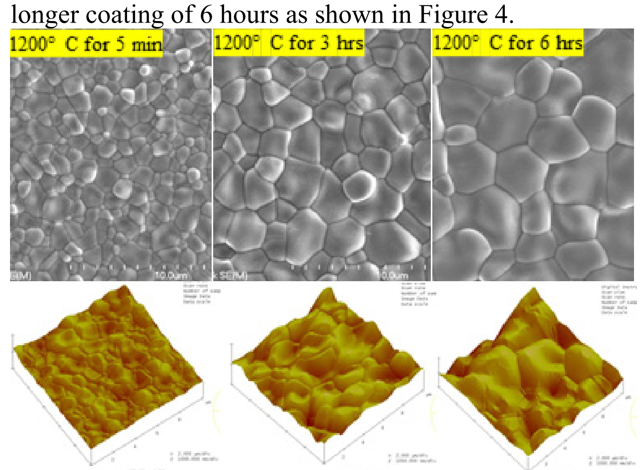

Figure 4: SEM and AFM images from NP samples coated at 1200 °C for 5 min, 3 hours and 6 hours. Scale for 10 µm×10 µm AFM images shown here are 2 µm/div along x-direction and 1 µm/div for z-direction.

AFM images (e.g. Figures 4) showed a clear variation in roughness. The roughness of coated NP samples from each experiment were compared in terms of the power spectral densities (PSD) from surface height data obtained from 50 µm × 50 µm and 10 µm × 10 µm AFM scans from 4–5 randomly selected areas as before [15]. The log-log plot of calculated PSD is shown in Figure 5. Since the area under the PSD gives the square of root mean square roughness, it shows that high spatial frequency surface roughness decreases with increase in grain growth. Longer coating at any temperature appears to increase the macroroughness.

XPS depth profile data was collected from pre-anodized and regular BCP samples coated at different conditions discussed above. Some of them from anodized samples are shown in Figure 6. It shows that there exists a plateau of almost constant tin concentration close to the surface, which is similar for coatings prepared under different conditions, and followed by a steady concentration drop,

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which could be caused by roughness, close to Nb_3Sn-Nb interface before the tin signal vanishes. Thickness of the coating was inferred from the depth profile data of tin. The thickness of coating varied from few hundred nm to several µm depending on the deposition conditions.

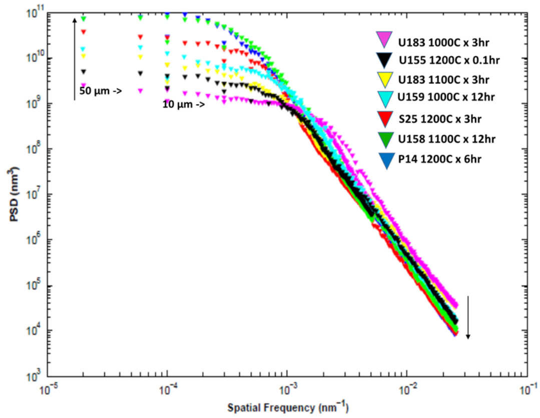

Figure 5: PSD comparison of samples coated with different deposition parameters.

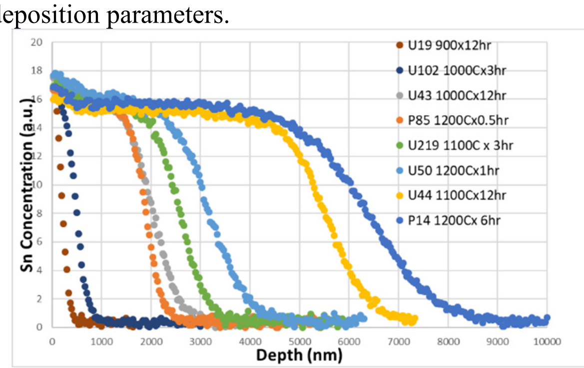

Figure 6: XPS depth profile from samples prepared under different deposition parameters.

The deposition temperature affects the coating in several ways. First, it determines the tin evaporation rate, which affects the arrival rate of tin vapor onto the niobium surface. Second, it effects the diffusion rate of tin into the substrate. Coating deposited at low temperatures (900 °C for 3 or 12 hours and 1000 °C for 3 hours) resembled our previous coatings produced with low tin evaporation [16], which indicates that the threadlike structures were caused by the low tin availability during the deposition. Smaller grains and patchy areas appeared on the surface with slightly higher tin availability. XPS depth profile indicates a little to no plateau region of Nb_3Sn close to the surface for such coatings with sharp drop of tin concentration at Nb_3-Sn Nb interface. Coatings at higher temperatures seem to avoid this issue, probably because of higher rate of tin arrival. Tin vapor at higher temperature may also have higher kinetic energy required to promote a uniform nucleation site density until well-connected Nb_3Sn grain networks are established. Note that [17] recommends higher temperature for tin source than the substrate temperature as a part of solution to improve coating uniformity. Deposition time is crucial to determine the coating growth, that is, the thickness of the coating. It is not clear yet quantitatively how the roughness and grain boundaries affect the performance of the cavity, but it appears that increase of one leads to decrease of another or vice versa. Longer coating at any temperature increases the macro-roughness by reducing the grain boundary density with grain growth as shown in Figure 7.

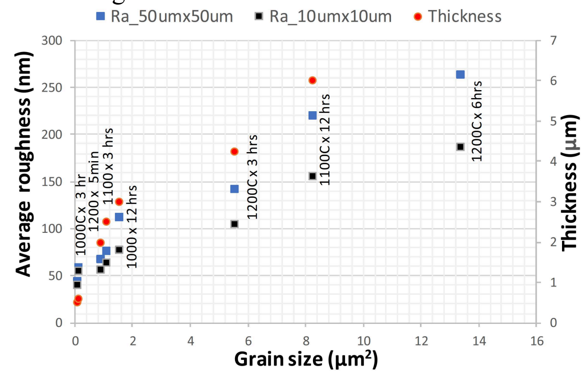

Figure 7: Observed relationship between grain size, coating thickness and surface roughness. Roughness values (R_a) were averaged values at 5 different location of the sample. Average grain sizes were estimated from 5–6 SEM images of 2000–3500 magnification. Thickness is estimated from XPS depth profiles.

CONCLUSION

Examination of Nb_3Sn coatings, deposited in the temperature range of 900–1200 °C for 3–12 hours, with different material characterization tools lead to the following conclusions.

1. Longer deposition time produces thicker coating and larger grain size.
2. Larger grain size correlates with increased surface macroroughness and thickness of the coating.
3. Composition of Nb_3Sn (24-25 at% Sn) does not depend on the deposition temperature in the range of 900–1200 °C within the accuracy of XPS detector.
4. Coating temperatures of (900–1000)°C are more prone to produce patchy regions with irregular grain structures.
5. NP samples showed patches more frequently than other samples.
6. Pre-anodization reduced the occurrence of thin film regions with irregular structures.

Based upon these observations, deposition temperatures above 1000 °C are recommended to avoid microstructural inconsistency like thread-like structure and thinly coated patchy regions in Nb_3Sn coating. Coating at higher temperature for short duration could be beneficial to balance the effect of roughness and grain boundaries to improve the performance of Nb_3Sn coated performance.

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