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STUDY OF CHEMICAL TREATMENTS TO OPTIMIZE NIOBIUM-3 TIN GROWTH IN THE NUCLEATION PHASE *

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Abstract

Niobium-3 tin (Nb_3Sn) is a high-potential material for next-generation Superconducting Radiofrequency (SRF) cavities in particle accelerators. The most promising growth method to date is based on vapor diffusion of tin into a niobium substrate with nucleating agent tin chloride ($SnCl_2$). Still, the current vapor diffusion recipe has significant room for realizing further performance improvement. We are investigating how different chemical treatments on the niobium substrate before coating influence the growth of a smooth and uniform Nb_3Sn layer. More specifically, this study focuses on the interaction between the $SnCl_2$ nucleating agent and the niobium surface oxides. In this paper, we present preliminary results of the comparison of the effect of different chemical treatments (with different pH values) on the tin droplet distribution on niobium after the nucleation stage of coating.

INTRODUCTION

Niobium-3 tin is a promising material for next-generation SRF cavities, due to its higher critical temperature and higher superheating field in comparison to other SRF materials. Many labs, including Cornell, Fermi Lab, Jefferson Lab, and KEK have continuing research and development projects focusing on improving Nb_3Sn growth. [1–9] The most promising growth method to date is based on vapor diffusion of tin into a niobium substrate with nucleating agent of tin chloride. The oxide layer of Nb_2O_5 on the surface of niobium plays an important role in the binding of the nucleating agent ($SnCl_2$) [2, 7, 10], and this research focuses precisely on optimizing the oxide layer to get a more uniform distribution of tin after the nucleation step.

Previous studies have shown Nb_2O_5 to be a very active catalyst for many processes as a result of its surface acidity and molecular binding sites [11, 12] . Different Nb_2O_5 surface structures and acidities have been shown to have varying abilities to bind to other molecules, making some structures better suited for our nucleation process. There are many ways to adjust the surface acidity, including water, solvent mixes, and surfactants. Temperature treatments can be used to modify the structure of the binding sites, with a higher temperature treatment leading to lower surface acidities.

In this study, we used varying solvent mixes to vary the surface acidity before nucleation, and changed the nucleation temperature to observe its influence on the binding of $SnCl_2$ onto our Nb_2O_5 surface. The ideal chemical treatment will yield a uniform and dense tin droplet distribution. After the nucleation step, we expect to see tin droplets in the nucleation sites, as well as a very thin Sn-Nb film. [7]

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PREPARATION OF SAMPLES

Pre-Coating Chemical Treatments

All samples were electropolished and anodized before the chemical treatments. The list of treatments and their corresponding pH value is shown in Table 1, with sample −1 being the non-treated sample.

Table 1: Summary of Chemical Treatments

Sample #	Chemical Treatment	pH
-1	-	
0	H_2O	
1	H_2O_2	4.7
2	$NaOH$	11
3	$NaOH$	9
4	NHO_3	3
5	NHO_3	5
6	HCl	5
7	HCl	3

Figure 1: Samples after chemical treatments, before coating.

Samples 0 through 8 are shown in Fig.1 starting from the top left, after the chemical treatments and before the coating. Note that they are all slightly different colors, due to the different chemical treatments.

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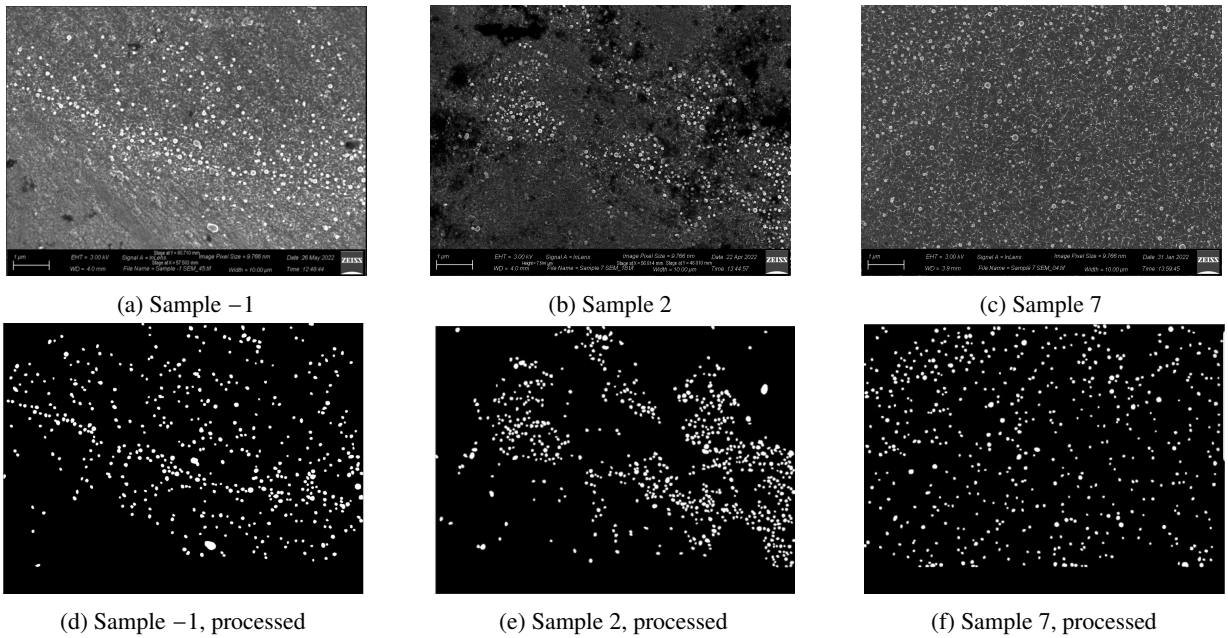

(a) Sample −1 (b) Sample 2 (c) Sample 7

(d) Sample −1, processed (e) Sample 2, processed (f) Sample 7, processed

Figure 2: Examples of SEM images for samples -1, 2 and 7 shown in subfigures (a) through (c), and their corresponding processed masks using ImageJ shown in subfigures (d) through (f).

Nb_3Sn Coating

The coating profile of the samples is shown in Fig. 3. The nucleating agent was heated at 435C, while the tin source was heated to a higher temperature in order to have an excess of tin during nucleation to minimize tin depleted regions. The coating of the samples was stopped after the nucleation step.

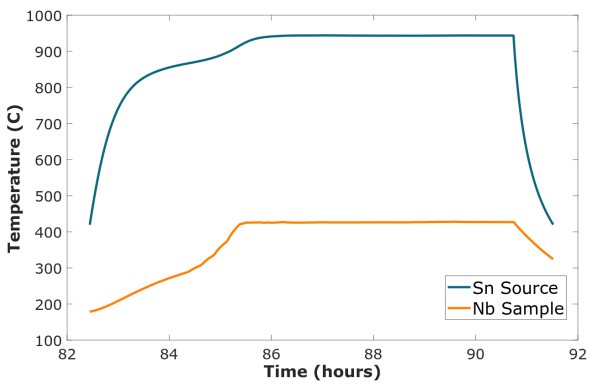

Figure 3: Temperature profile for Nb_3Sn vapor diffusion based growth. Coating was stopped after the nucleation step.

CHARACTERIZATION METHODS

In order to determine the optimal chemical treatment, we used surface characterization techniques of SEM (Scanning Electron Microscope) and EDS (Electron Dispersive Spectroscopy) to image the nucleated samples, and then used the image processing software ImageJ [13] for the processing of the images.

Analyzing Uniformity of Tin Droplets

As a qualitative measure of the uniformity of the nucleated tin "droplets" distribution on the niobium substrate, we took SEM images of multiple 10 µm wide regions on each sample. These images were processed using ImageJ software, with the StarDist plugin. Examples of one SEM image and its corresponding processed image for each sample analyzed to date is shown in Fig. 2. To analyze the uniformity of the tin droplets on our samples, we used a Nearest Neighbor Macro on ImageJ on the processed images to find the average distance from the six nearest neighbors for each droplet on the images. The statistics of the average distance between nearest neighbors is used as a qualitative metric to measure how uniform each sample is. More specifically, we use the standard deviation of the distribution of these distances. The smaller the standard deviation is, the fewer clusters are found on the sample.

Another figure of merit for the quality of each sample is the density of the droplets. When comparing two samples with a similar standard deviation of the six nearest neighbors metric, we deduce that the most promising coating is the one with the higher density of tin droplets.

EDS Analysis of Tin Droplets

In order to confirm that the droplets in the SEM images are really tin, and to quantify the Sn-Nb thin film we were expecting, we used EDS to get the average atomic percentages of selected elements, in our case tin and niobium.

Using the same processing software as for the previous section, we calculated the % area covered by the white droplets shown in Fig. 2 (d)-(f), and compared it against the % ratio of tin to niobium from the EDS scan.

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PRELIMINARY RESULTS

The results from the analysis of the distribution of the average distance of six nearest neighbors are plotted in Figure 4 for samples -1, 2 and 7. Sample 2 has the biggest standard deviation, which corresponds to more clusters in the sample. The density of droplets for sample 2 is 5.49 droplets per μm^2. The untreated sample (-1) and the low pH sample 7 have similar standard deviations, however, sample 7 has a higher density of 7.56 in comparison to 4.66 droplets per μm^2 of the untreated sample, making it the most promising treatment so far.

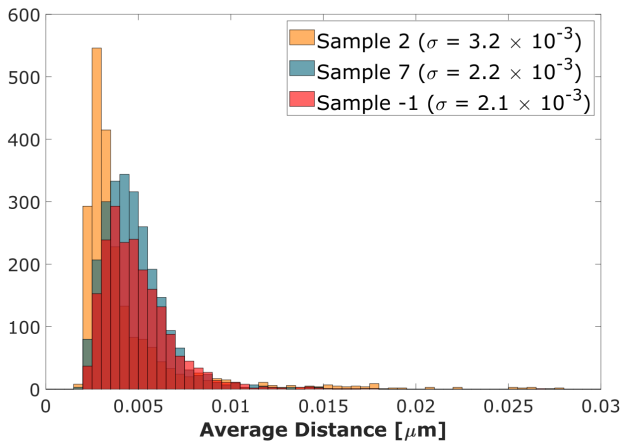

Figure 4: Histogram of cumulative average distance of 6 nearest neighbors, for samples 2, 7 and -1. Statistics was taken over 5 SEM images of width 10 µm for each sample.

The preliminary results for the ratio of tin to niobium are plotted in Figure 5. The non-zero y-axis intercept indicates the presence of a Sn thin film, observed on all three samples. Note that the accelerating voltage used for EDS on samples -1 and 2 is 20kV, while the one for sample 7 was 10kV. Hence, we can only conclude that the thin film on sample 2 is of lower concentration than the untreated sample. Next steps entail taking EDS maps on all samples using the lower voltage, as that doesn't probe as deep into the bulk niobium.

CONCLUSION

We have laid groundwork to qualitatively compare the effect that different chemical treatments of the niobium substrate have after the nucleation step of vapor diffusion based Nb_3Sn growth. One of these methods is comparing statistics of the average distance between the six nearest neighbors of the nucleated droplets. Preliminary results indicate a difference in the distribution of nucleation sites between a low and high pH, the lower pH value having a more uniform distribution. Additionally, the lower pH sample has a higher droplet density compared to the untreated sample, making it the most promising treatment so far. Future work entails taking more SEM and EDS data to determine optimal Nb substrate preparation, which will then be tested on a Nb_3Sn coated cavity.

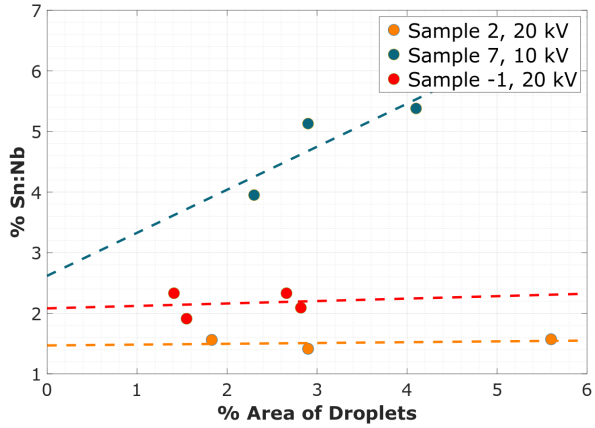

Figure 5: Plot of EDS ratio of tin to niobium versus the calculated % area covered by the droplets in the processed SEM images.

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