

INVESTIGATION OF STRUCTURAL DEVELOPMENT IN THE TWO-STEP DIFFUSION COATING OF Nb₃Sn ON NIOBIUM*

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Abstract

The potential for higher operating temperatures and increased accelerating gradient has attracted SRF researchers to Nb₃Sn coatings on niobium for nearly 50 years. The two-step tin vapor diffusion: nucleation followed by deposition appears to be a promising technique to prepare Nb₃Sn coatings on interior cavity surface. We have undertaken a fundamental materials study of the nucleation and deposition steps. Nucleation was accomplished within parameter ranges: 300 - 500 °C, 1 - 5 hrs duration, 5 mg - 1 g SnCl₂ and 1g Sn. The resulting deposit consists of (< 10%) coverage of tin particles, as determined by SEM/EDS, while XPS and SAM discovered extra tin film between these particles. Preliminary results by EBSD show no evident effect of substrate crystallography on the crystallography of the final coating. Substantial topography was found to develop during the coating growth.

INTRODUCTION

Discovered in 1954 [1], Nb₃Sn has the potential to replace traditional niobium in superconducting radio frequency (SRF) cavities. Because both the critical temperature and superheating field are nearly twice that of niobium, Nb₃Sn promises higher operating temperature and accelerating gradient than niobium SRF cavities, resulting in significant cost reduction. Despite these advantages, Nb₃Sn is a brittle material with low thermal conductivity, so its application must be restricted to coating form. Complicated cavity shapes limit the types of techniques available to prepare Nb₃Sn coatings.

The most successful coating technique thus far is tin vapor diffusion, developed at Siemens AG in the 1970s [2], and further developed at Wuppertal University [3]. The majority of research institutions currently working to develop Nb₃Sn-coated SRF cavities have adopted this technique [4-6]. The basic procedure consists of two steps: nucleation and deposition. First, tin chloride is evaporated at about 500 °C, depositing tin on the niobium surface. These tin deposits act as nucleation sites, which are assumed to grow with the influx of tin vapor during deposition at higher temperature. Deposition temperature suitable to form Nb₃Sn phase is determined by the Nb-Sn binary phase diagram [7]. An example of the Nb₃Sn coating process at Jlab is shown in Figure 1.

Although tin vapor diffusion is a promising technique for future development of Nb₃Sn SRF cavities, fundamen-

tal material studies are still needed to better understand the coating process. The goal of this research is to refine this coating technique by conducting more thorough investigations of the nucleation and deposition processes. Accordingly, we discuss the results from both nucleation experiments and complete coating experiments.

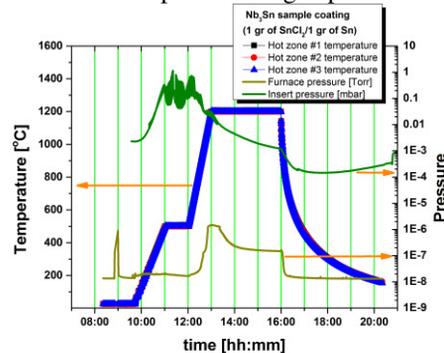


Figure 1: Temperature profile used for coating Nb₃Sn onto niobium samples. The nucleation process occurs at the first temperature plateau of 500 °C and deposition proceeds at the 1200 °C temperature plateau.

EXPERIMENTAL DESCRIPTION

High purity niobium coupon samples were prepared by electric discharge machining (EDM) 3mm-thick sheet material which is the same type of material used to fabricate SRF cavities at Jlab. All samples were subjected to buffered chemical polishing (BCP) with an expected minimum removal of 50 μm, followed by metallographic polishing, also known as nanopolishing (NP).

A detailed description of the Jlab deposition system used in this work is available in [4]. The setup of this experiment is similar to the setup described in our previous work [8]. One gram of tin (~3 mg/cm²) and one gram of tin chloride were packaged in niobium foil and placed inside a sample chamber. After mounting sample coupons inside the chamber, both ends of the chamber were covered either by niobium foils or niobium plates before it was installed in the furnace insert. Once the insert had been pumped down to a pressure of 10⁻⁵ – 10⁻⁶ Torr, the heating profile was initiated. During nucleation experiments, the temperature inside the insert was increased at a rate of 6 °C /min until it reached the desired nucleation temperature. The time period for which this temperature was maintained depended on the experiment.

A field emission scanning electron microscope (FE-SEM) with energy dispersive x-ray spectroscopy (EDS) was used to examine the nucleated samples. SEM images were taken and visible features were analyzed with EDS.

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We used a commercial AFM in tapping mode to obtain information about surface morphology at higher resolution. Surface sensitive elemental analysis was performed using x-ray photoelectron spectroscopy (XPS) and, for some samples, scanning Auger microscopy (SAM). Electron backscatter diffraction (EBSD) was used to extract crystallographic information.

NUCLEATION STUDIES

Depending on the experiment, the amount of tin chloride, nucleation temperature, and nucleation time were varied either individually or in some combination. First results were reported briefly in [9]. The nucleation temperature was varied from 300 °C to 500 °C with a constant nucleation time of one hour. For the nucleation temperature of 300 °C, < 50 nm sized particles were observed on the niobium surface. EDS detected only niobium, while XPS shows the presence of tin. This discrepancy arises from the difference in depth resolution of these two techniques. Larger micron sized tin particles often appeared when the sample was treated at 400 °C. The surfaces created by a nucleation temperature of 450 °C and 500 °C were similar and contained tin particles visible in SEM images (Figure 2). EDS was unable to detect any tin in between these visible tin particles. Calculated surface coverage of these particles from SEM images was always less than 10%. XPS analysis on the other hand showed an average of (20-30) % tin in samples prepared with nucleation temperature of 400 °C or higher. XPS analysis did not find any chlorine in any of those samples.

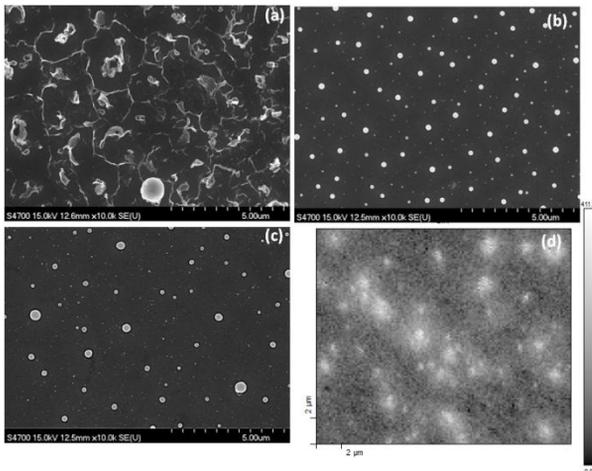


Figure 2: SEM images of samples with a nucleation time of one hour at various nucleation temperatures: (a) 400 °C, (b) 450 °C, (c) 500 °C. EDS was only able to identify tin from bright circular features. SAM elemental mapping of tin coverage from the sample treated at 500 °C for one hour is shown in (d). Note that surface produced after one hour at 400 °C appears very different.

We further examined samples from the experiment with nucleation temperature of 500 °C for one hour using high resolution SAM. Elemental mapping of tin in the SEM image with SAM (Figure 2d) clearly shows that there is tin on the surface in between the visible particles in SEM image.

It was found that after only five minutes at 500 °C, some tin particles (~500 nm) were already produced. Figure 3b shows the surface was covered with stringy features. Comparing the results obtained after one hour at 500 °C (Figure 2c) to four hours at same temperature (Figure 3a), it appears that more tin particles were produced with the longer nucleation time, but the average size of these particles were smaller. EDS was only able to detect tin from particles visible in the SEM image, however XPS analysis revealed more tin than was accounted for by EDS.

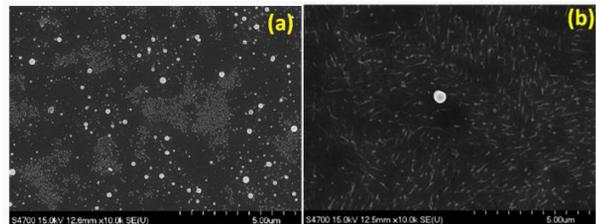


Figure 3: SEM images of samples obtained from experiments with a nucleation temperature of 500 °C and nucleation time of (a) 4 hours and (b) 5 minutes.

We replicated the Cornell nucleation protocol (7 $\mu\text{g}/\text{cm}^2$ of tin chloride, 500 °C for five hours, temperature ramp at 3 °C/min) and compared the result to that of Jlab nucleation protocol (3 mg/cm^2 of tin chloride, 500 °C for one hour, temperature ramp at 6 °C/min). Figure 4a shows that Cornell protocol with lower amount of tin chloride produces a uniform distribution of particles that are smaller than the particles observed with the Jlab protocol. The SAM tin elemental mapping corresponding to the Cornell nucleation protocol is shown in Figure 4b. SAM and XPS analysis show comparable tin coverage in nucleated samples obtained from both nucleation protocols. Although both protocols result in similar tin coverage on the niobium surface, it appears that the Jlab protocol also produces larger tin particles due to increased amount of tin chloride. It is suspected that the longer nucleation time in the Cornell protocol contributes to more uniform coverage of tin particles with a small amount of tin chloride. Note that the longer nucleation time of four hours with Jlab protocol also resulted in more surface coverage of tin particles (Figure 3a).

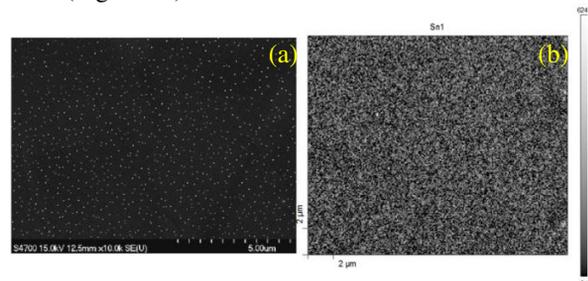


Figure 4: (a) SEM image of nucleated surface obtained by using Cornell recipe. (b) SAM elemental mapping of tin.

STRUCTURAL DEVELOPMENT

The coating process was interrupted at different stages with the intention of gaining insight into the structure

development of Nb₃Sn during the coating process. Results obtained after the nucleation stage of 500 °C for one hour was discussed in the previous section. The second interruption at one minute after reaching 1200 °C revealed that small grains (~100 nm) had already formed all over the surface (Figure 5b) with a few tin particles. An XPS scan of the surface showed ~ 27 at% ratio of tin to niobium, whereas EDS measured ~ 20/80 at% ratio of tin to niobium. After one hour at 1200 °C, the coating process was interrupted again. At this point, significant grain growth with the absence of tin particles was observed (Figure 5c) with a grain size of ~0.25 μm. EDS measured ~21 at% tin for the coating. Completion of the coating process after three hours at 1200 °C shows grain growth from ~0.25 μm to ~1 μm (Figure 5d) and ~24 at% tin. We also found

that roughness increases with grain growth during the deposition stage (Figure 5).

Cross-sections of the coated samples were prepared using focused ion beam (FIB) after applying a protective layer of platinum to the surface. The cross-sections were then polished using ion mill. An EBSD image captured the structure of the final coating. The orientation image map (OIM) is shown in Figure 6. Columnar grains were normally observed extending from the surface of the Nb₃Sn layer all the way to the Nb₃Sn-Nb interface. Some smaller non-columnar grains were also present (Figure 6a). We did not find any explicit evidence that substrate grain orientation influences the grain orientation of final coating.

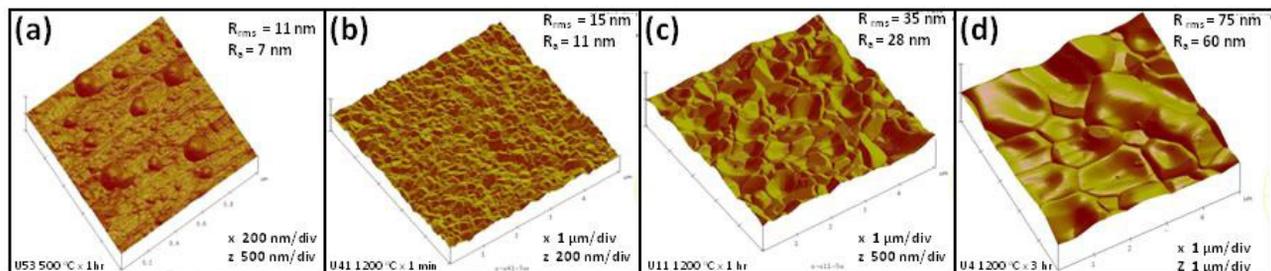


Figure 5: AFM images shows grain growth and topography evolution during the coating process. (a) Sample treated at 500 °C for one hour. The scan size is 1 μm x 1 μm. (b) Sample treated at 1200 °C for one minute, (c) 1200 °C for one hour and (d) 1200 °C for three hours. The scan size for images (b) – (d) is 5 μm x 5 μm.

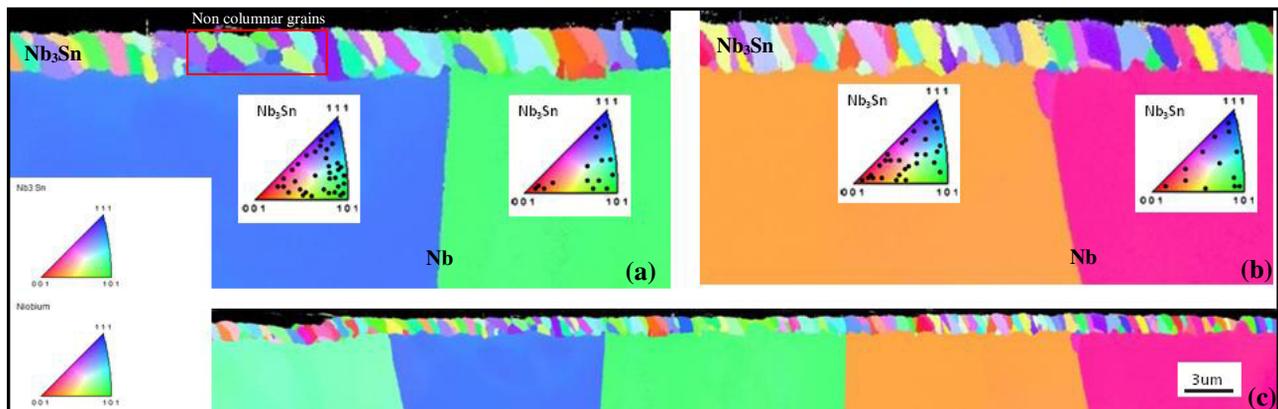


Figure 6: EBSD image of the cross-section from sample U3 is shown in (c). Smaller grains on the top are Nb₃Sn. Larger grains at the bottom are Nb. Images (a) and (b) are magnified areas from (c). Approximate orientations of Nb₃Sn grains on each Nb grain are shown with inverse pole figure using assigned color for each grain. Each dot represents an individual Nb₃Sn grain.

CONCLUSION

We studied the surfaces obtained with different sets of nucleation parameters by using different characterization tools. No chlorine was detected after any of the nucleation experiments. XPS and SAM analysis of nucleated samples indicated the presence of tin film in between tin particles, which were seen in SEM. The amount of tin chloride was not found to be crucial for achieving uniform tin coverage on the niobium substrate surface, although larger tin particles were produced when a larger amount of tin chloride was used. Surface topography was found to

develop substantially during the coating growth at deposition stage. Preliminary results from EBSD examination of the coating cross-section have found no evident effect of substrate orientations into the orientation of final coating.

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REFERENCE

- [1] B.T. Matthias, T. H. Geballe, S. Geller, and E. Corenzwit, *Phys. Rev.*, 95:1435-1435,1954.
- [2] B. Hillenbr and H. Martens, *J. Appl. Phys.*, 47(9):4151-4155, 1976.
- [3] G. Muller et al., in *Proc. EPAC'96*, Barcelona, Spain 1996, paper WEP002L, pp. 2085-2087.
- [4] G.V. Eremeev, W. A. Clemens, K. Macha, H. Park, and R. S. Williams, in *Proc. IPAC'15*, Richmond, USA, 2015, paper WEPWI011, pp. 3512-3514.
- [5] S. Posen et al., in *Proc. SRF'15*, Whistler, Canada, 2015, paper TUPB048, pp.678-680.
- [6] S. Posen and M. Liepe, in *Proc. SRF'13*, Paris, France, 2013, paper TUP087, pp.666-670.
- [7] J. P. Charlesworth, I. Macphail, and P. E. Madsen, *J. Mat. Sci.*, 5, pp. 580-603 (1970).
- [8] U. Pudasaini, G. V. Eremeev, M. J. Kelley, and C. E. Reece, in *Proc. SRF'15*, Whistler, Canada, 2015, paper TUPB054, pp. 703-707.
- [9] U. Pudasaini, G. V. Eremeev, M. J. Kelley, and C. E. Reece, in *Proc. LINAC'16*, East Lansing, Michigan, USA, 2016, paper THOP01.