TOWARD STOICHIOMETRIC AND LOW-SURFACE-ROUGHNESS Nb₃Sn THIN FILMS VIA DIRECT ELECTROCHEMICAL DEPOSITION*

Z. Sun[†], G. Gaitan, M. Ge, K. Howard, M. U. Liepe, R. D. Porter, T. Oseroff
CLASSE, Cornell University, Ithaca, NY, USA
T. Arias, Z. Baraissov, M. Kelly, D. Muller, J. Sethna, N. Sitaraman
Department of Physics, Cornell University, Ithaca, NY, USA
K. D. Dobson, Institute of Energy Conversion, University of Delaware, Newark, DE, USA

Abstract

Reducing surface roughness and attaining stoichiometry of Nb₃Sn superconducting films are required to push their superheating field to the theoretical limit in SRF cavities. As such, we explore direct electrochemical processes that minimize involving foreign elements to deposit high-quality Sn, Nb, and Nb$_x$Sn films on Nb and Cu surfaces. These films are then thermally annealed to Nb₃Sn. We find that smooth Sn pre-depositions via electroplating on Nb surfaces significantly reduce the average roughness of resultant Nb₃Sn to 65 nm. Structural and superconducting properties demonstrate a Nb₃Sn A15 phase with a stoichiometry of 25 at% Sn. This process has been scaled-up to a 3.9 GHz cavity. Moreover, preliminary results on electroplating on Cu surface show that Nb plating undergoes a slow growth rate while subsequent Sn plating on the plated Nb surface can be controlled with varied thickness. The Nb plating process is currently being optimized.

INTRODUCTION

Nb₃Sn superconducting films that are used on the inner surface of SRF cavities seek to advance the accelerating gradient up to 100 MV/m and allow operating at 4 K with a lowered cryogenic cost, enabled by a doubled superheating field (~400 mT) and a high critical temperature (18 K) of this material as compared to conventional niobium [1]. However, the RF performance of vapor-diffused Nb₃Sn cavities currently reaches accelerating gradients of up to 24 MV/m [2], significantly lower than the theoretical predicted limit of 100 MV/m. To overcome this big gap, researchers have identified two major issues in Sn vapor diffusion, the state-of-the-art method for making Nb₃Sn. One issue is the large surface roughness that is mainly induced by variation in grain size due to non-uniform nucleation events [3,4]. The peak regions result in field enhancement while the valley regions are enabling premature for vortex nucleation [5]. The second issue is Sn depletion regions that are frequently observed in the film [4,6] due to insufficient Sn supply during the vapour diffusion growth [7]. The off-stoichiometry degrades the critical temperature of Nb₃Sn, e.g., $T_c \approx 10$ K at 20 at% Sn [7]. Thus, it is desirable to develop a new deposition process that revolves these issues.

Our strategy is pre-deposition of a smooth Sn film on a Nb substrate and then thermal conversion to Nb₃Sn. Several advantages include promotion of uniform distribution of nucleation events to lower surface roughness and supplying sufficient Sn to satisfy the kinetic requirement for Nb₃Sn stoichiometry. To deposit the initial Sn film, an electroplating method is of interest due to the low cost and capability to scale up to cavities. Previous studies on Sn plating on Nb surfaces rely on a Cu seed layer [8] or bronze [9]. Here, we intend to avoid any Cu contamination and choose a different path via optimization of solution chemistry. Our earlier work [10-13] have demonstrated the success of stoichiometric Nb₃Sn deposition with extremely low surface roughness through Sn electroplating.

In this work, we continued the optimization and characterization of the electroplating-based Nb₃Sn, together with a comparison with vapor-diffused Nb₃Sn. We improved the understanding of the growth mechanism that is critical to future film design. Furthermore, we optimized the Sn plating process on a 3.9 GHz cavity, which is a main focus of this paper.

In addition, we are developing Sn and Nb electroplating processes on Cu substrates since Cu cavities are cost-effective and exhibit better thermal properties. Preliminary results are also discussed.

METHODS

A three-electrode electrochemical deposition system was installed at Cornell as shown in Fig. 1. The 3.9 GHz cavity was connected to the working electrode while a cylinder mesh Pt counter electrode and a saturated calomel reference electrode were inserted inside the cavity.
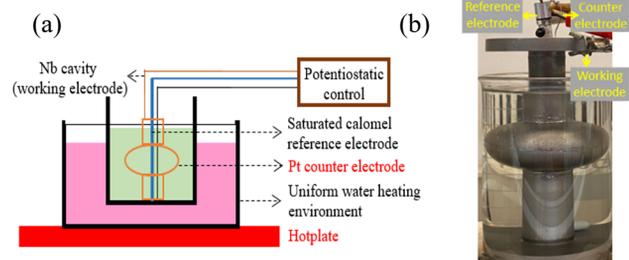

Figure 1: (a) Schematic and (b) picture showing the electrochemical deposition system at Cornell. Note that water heated bath and temperature feedback control are not shown in the picture.

Electroplating processes are developed on both Nb and Cu surfaces: Sn film on Nb surface and Sn/Nb multilayer films on Cu substrate. The Sn plating process has been demonstrated both in sample studies and on the cavity scale, while the Nb plating process is being optimized on Cu substrate samples. Before electroplating, Nb substrates were electropolished and Cu substrates were chemically polished.

The electroplating parameters investigated were the plating temperature, solution chemistry, plating potentials, plating current, ph-values, and stirring conditions. After plating, films were furnace annealed to Nb_3Sn using the heating profile from vapor diffusion [3].

Surface, structural, chemical, and atomic characterization has been extensively performed. Scanning electron and atomic force microscopes (Zeiss Gemini 500 SEM and Asylum MFP-3D AFM) were used to examine the surface morphology and quantify the surface roughness. Depth profiling via X-ray photoelectron spectroscopy (XPS) and composition mapping via energy-dispersive X-ray spectroscopy (EDS) provide the stoichiometry and impurity information. X-ray diffraction (Rigaku XRD) and scanning transmission electron microscopy (FEI F20 STEM) were used to probe the grain and atomic information. The critical temperature of Nb_3Sn was determined by a Quantum Design Physical Property Measurement System.

RESULTS AND DISCUSSION

Surface Roughness and Stoichiometry

The electroplated-Sn converted Nb_3Sn films exhibit extremely low surface roughness and pure stoichiometry. Figure 2a shows a visual comparison of surfaces from vapor diffusion and electroplating. Clearly, samples from electroplating are smoother. Quantification of average roughness by AFM shows a low surface roughness of 60 nm that is 5 times reduction as compared to vapour diffused samples. Other roughness parameters (root mean square roughness and absolute peak-to-valley height) confirm the improvement of surface profile by pre-depositing Sn films. Note that Fermilab, KEK, and Cornell recently reported "shiny" vapor diffused Nb_3Sn with average roughness of ~100 nm.
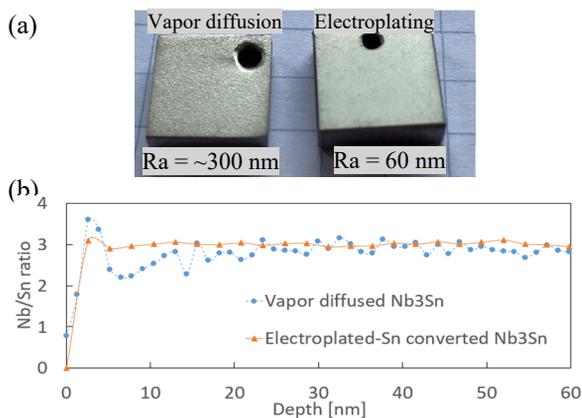

Figure 2: Comparison of (a) surface roughness and (b) stoichiometry between vapor diffusion and electroplating.

Besides the low surface roughness, a pure stoichiometry is also achieved owing to sufficient Sn supply for electroplated samples. Figure 2b shows a comparison of local stoichiometry as a function of depth for both films. A constant 3:1 Nb/Sn ratio was observed for electroplated samples except in the surface oxide region, while vapor diffused samples show a Nb/Sn ratio that fluctuates with depth. Local composition mapping by an EDS probe under STEM confirmed the uniform stoichiometry at the surface region (>500 nm in depth) of electroplated samples.

Scale Up Sn Electroplating to a 3.9 GHz Cavity

With the two benefits, pure stoichiometry and low surface roughness, the Sn electroplating process was scaled up to a 3.9 GHz cavity. Here, several considerations are listed to compare cavity-scale plating and sample-scale plating. With these considerations, the Sn electroplating process was re-optimized on the cavity scale.

- How to maintain a uniform heating?
- How to overcome the PH value variation when mixing large volume solutions, indicating a solution chemistry change?
- What is the impact of stirring?
- How to overcome the local current density variation due to a complex cavity shape?
- What is the impact of electrode position?

The first and important optimization is to achieve a uniform heating process at the optimal plating temperature. The plating temperature is critical in the Sn plating process. As shown in Fig. 3, the uniform Sn films were only achieved at the optimized temperatures while Cl-rich dendrites were obtained near room temperatures. To improve the heating uniformity, a heated water bath and a temperature feedback control were applied in the sample plating. However, when mixing large volume solutions, it is difficult to reach the target temperature because the hotplate only contacts with the bottom of a large beaker while the heat dissipation to the environment is large. Also, with a long-hour heating, the solution composition would be changed due to water evaporation. To improve the heating process, we modify the heating system by adding a heating belt around the beaker together with temperature monitoring at different locations using thermocouples. Also, we plan to optimize the effect of stirring that was not used in the sample plating due to the interruption of plating current in the solution.
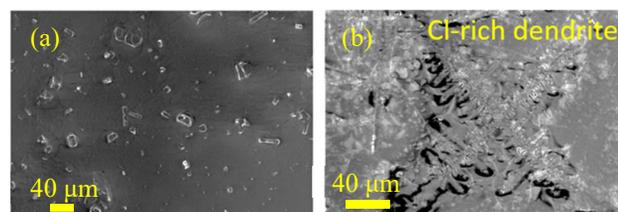

Figure 3: Effect of plating temperature. Surface SEM images of samples electroplated from (a) optimized temperature and (b) near room temperature.

The second optimization is to tune the plating potential and current. In a three-electrode system, the plating potential determines the electrochemical reaction while the plating current that is affected by plating potentials has a large impact on the film quality. In the cavity-scale plating, however, a dramatic change of plating current was observed when the plating voltage was slightly adjusted. Due to a complex cavity shape, the local current density greatly differs between the sharp, curved, and flat regions. Figure 4 shows, after the plating, Sn particles were observed on the iris region while Sn films were deposited on the equator region. Thus, the plating current was optimized via adjusting plating voltages at the step of microvolts. Further optimization would rely on fixing the electrode positions so that an effective comparison of plating current can be performed between baths in a three-electrode system.
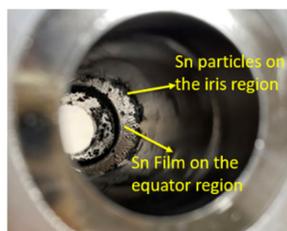

Figure 4: Effect of local current density. Picture of the inner surface of an electroplated 3.9 GHz Nb cavity at relatively high plating potentials.

The solution chemistry and ph-values are also important to this electroplating process. $SnCl_2$ precursors would generating a white cloudy solution (Fig. 5a) due to the chemical reaction with water. In both cavity- and sample-scale platings, a transparent solution (Fig. 5b) was achieved together with a slight ph-value change. Besides actively monitoring the ph-value during electroplating, the cavity-scale plating adopted the same solution chemistry as sample-scale plating.
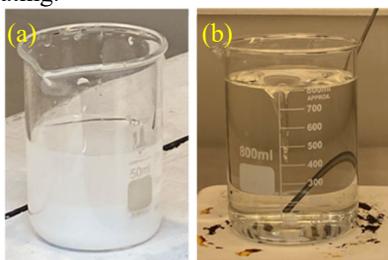

Figure 5: Effect of solution chemistry. Pictures of (a) $SnCl_2$ in water and (b) typical cavity plating solution.

With these improvements, the Sn plating test was first performed on the cavity outer surface. Grey-color films with shiny Sn crystals were observed on the equator region during the electroplating. After the plating and ultrasonic in methanol for 30 min, a swipe test shows robust Sn films on the Nb surface (Fig. 6), suggesting a good adhesion property. This result matches with the tape and swipe tests performed after sample-scale plating [10].
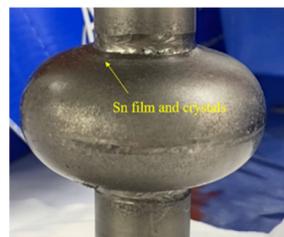

Figure 6: Sn electroplating test on the outer surface of a 3.9 GHz Nb cavity.

After the outer surface test, the same plating parameters were applied in the inner surface plating together with the same plating bath. As shown in Fig. 7, before the plating, the pre-electropolished surface was shiny, while after the plating, Sn films were observed on the cavity inner surface. A film edge on the tube region, which was the plating solution edge, is marked in Fig. 7b. This result demonstrates the feasibility and success of scaling up the Sn electroplating process to a cavity level.
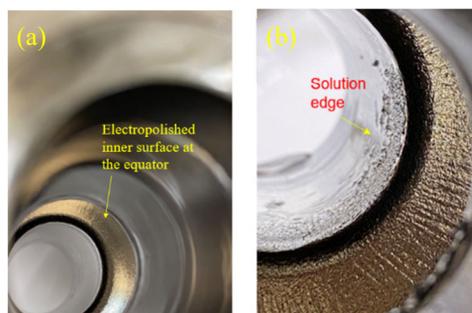

Figure 7: Sn electroplating on the inner surface of a 3.9 GHz cavity: (a) before and (b) after the electroplating.

Preliminary Results on Sn/Nb Multilayer Electroplating on the Cu Surface

In order to achieve electroplating-based Nb_3Sn on Cu cavities, water-free electroplating processes are being developed. As shown in Fig. 8a, a Nb film was first electroplated on the Cu surface. A porous morphology consisting of ~500 nm grains was observed. Also, the deposition rate is small (a few micrometers per day). New Nb plating processes are being investigated to achieve a better Nb barrier layer for the subsequent Sn electroplating.

Sn deposition from water-free baths is shown in Fig. 8b. The Sn film was electroplated on the plated Nb/Cu surface. The kinetics of Sn plating is favored and the deposition rate is large. Current results show that ~2 μm sized Sn grains scattered in the Sn film.
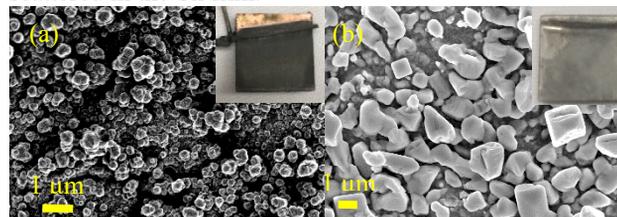

Figure 8: Surface morphology of electroplated (a) Nb and (b) Sn/Nb films on the Cu surface from water-free baths. Insets show the pictures of electroplated samples.

CONCLUSIONS AND FUTURE WORK

In summary, stoichiometric Nb_3Sn with low surface roughness was demonstrated using Sn electrochemical deposition followed by thermal conversion. Characterization of the stoichiometry and surface roughness for plated-Sn converted Nb_3Sn, together with comparison with vapor-diffused Nb_3Sn, is provided, and a thorough material analysis can be found in References [10-13].

This Sn electroplating process was successfully demonstrated on a 3.9 GHz Nb cavity after re-optimization of plating temperature and local plating current without changing the solution chemistry. Further optimization using electrode fixtures will be performed, and an RF result is expected in the future.

In addition, Nb/Sn multilayer electroplating processes are being optimized on the Cu surface.

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