STOICHIOMETRIC Nb3Sn IN FIRST SAMPLES COATED AT CORNELL*

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Abstract

A cavity coated with the superconductor Nb3Sn theoretically will be able to reach more than twice the maximum accelerating field of Nb in a cavity under the same operating conditions and will have a much lower BCS surface resistance at a given temperature. The SRF group at Cornell has recently developed facilities to fabricate Nb3Sn on Nb. The first samples have been coated, and several tests have been performed to characterize them. Results presented include SEM images of the surface, anodization tests, a critical temperature measurement, a test for RRR degradation, and stoichiometry measurements using EDS and XPS.

INTRODUCTION

After years of development, niobium SRF cavities are now being fabricated that are limited in gradient by the RF critical field, not multipacting, thermal instability, field emission, or high field Q slope. To reach even higher gradients, new materials must be used that will allow the RF surface to tolerate higher magnetic without quench. Theory [1] predicts that coating a cavity with Nb3Sn will allow it to reach twice the accelerating gradient of a niobium cavity. Nb3Sn also benefits from a critical temperature that is nearly twice as high as that of niobium, which allows cavities coated with Nb3Sn to operate with quality factors far exceeding those of Nb cavities at the same temperature.

Figure 1: The best results obtained at University of Wuppertal for 1.5 GHz cavities vapor-diffusion coated with Nb3Sn. From [4].

The great potential of Nb3Sn-coated cavities has already been shown in the results obtained by researchers at University of Wuppertal in the 1980s-90s [2] [3]. They produced cavities with quality factors of 10^11 at 2 K and accelerating gradients competitive with the gradients of niobium cavities produced at the time. Some vertical test results are shown in Figure 1. Guided by their work, facilities at Cornell have been developed to fabricate Nb3Sn films on niobium. This paper discusses those facilities and the first results obtained.

COATING PROCESS

The vapor diffusion coating process was based on [2]. A UHV furnace containing a niobium substrate (e.g. a cavity), a tungsten crucible containing 99.999% Sn pellets, and a tungsten crucible containing a small amount of SnCl2 is evacuated and degassed at 200°C. The coating chamber, shown in Figure 2, is self-contained to avoid contaminating the furnace with tin. The valves to the pumps are then closed and the temperature is raised to 500°C, at which point the vapor pressure of SnCl2 is high enough for it to create tin nucleation sites on the Nb surface. After 5 hours, the furnace temperature is raised to 1100°C, and a heater raises the temperature of the Sn slightly higher, to 1200°C. The elevated temperature from the heater increases the vapor pressure of tin in the coating chamber. The furnace temperature and the tin temperature control respectively the rate of interdiffusion of niobium and tin in the sample and

Figure 2: The Nb3Sn coating chamber being inserted into the UHV furnace (left) and a cross section (right) showing the tin crucible surrounded by the heater and the substrate suspended above. The red circles represent thermocouples for temperature monitoring.
the rate at which tin arrives at the sample surface, and they
can be varied to affect the composition of the alloy pro-
duced. After 3 hours the heater is turned off, and the re-
mainning tin vapor in the chamber is given 30 minutes to
reach a surface and diffuse in, so as to avoid unreacted tin
on the RF surface. Finally, the furnace is turned off and
backfilled with nitrogen gas when it is cool.

The Cornell procedure will include preparation tech-
niques that have been developed in the last two decades.
Already, Nb substrates—currently only flat samples have
been coated, not full cavities—are HPR’d prior to coating.
Soon, Nb substrates will be EP’d to give a smooth RF sur-
face prior to coating, and also baked at 120°C.

NON-RF ANALYSIS OF NB₃Sn COATINGS

Several different techniques have been employed to
study the composition of the first coated samples produced.
Only RF tests will determine if the coating process is satis-
factory; these tests are intended just to confirm that Nb₃Sn
is indeed produced using the apparatus. In the future, these
tests will hopefully also serve to correlate RF performance
to surface qualities.

One of the samples was anodized to test the surface com-
position. In this procedure, the sample is placed in 10%
NH₄OH and a 75 V potential is applied between it and an
anode. The thickness of the oxide that grows gives it a
color that is characteristic of the material on the surface.
Any unreacted tin will turn yellow, niobium will turn blue,
and Nb₃Sn will turn pink-purple [5]. The color of the sam-
ple, shown in Figure 3, indicates that the material on the
surface is Nb₃Sn.

![Figure 3: Nb₃Sn-coated sample (left) and an identical sam-
ple after anodization in NH₄OH at 75 V (right). The pink-
purple color indicates Nb₃Sn phase on surface.](image)

Images obtained using a LEO 1550 FESEM of the first
samples coated are shown in Figure 4. Micron-sized grain
growth was observed similar to that in images published by
the group at Wuppertal.

To quantify the composition of the Nb₃Sn layer, an en-
ergy dispersive x-ray (EDX) analyzer connected to the FE-
SEM was used. Firing 10 keV electrons at the sample and
measuring the spectrum of x-rays emitted (shown in Fig-
ure 5), it probes the relative abundance of Nb and Sn up to
approximately 0.5 microns into the surface [6]. An abun-
dance of 24.2±0.5 atomic percent tin (atm%Sn) was mea-
sured (uncertainty from [7]).

![Figure 4: SEM images of Nb₃Sn produced at Wuppertal in
1996 (left) and at Cornell in 2011 (right).](image)

![Figure 5: EDX spectrum of Nb₃Sn sample indicates com-
position ~24.2 atm%Sn.](image)

Nb₃Sn is the name given to the A15 phase of the Nb-
Sn system, which has a composition ranging from approxi-
mately 18 to 25 atm%Sn. A. Godeke has reviewed the
strong variation in the properties of the alloy with com-
position [9]. For example, the variation of $T_c$ and $H_{c2}$ with
composition is shown in Figure 6. The data indicate that
higher Sn content will yield a higher $T_c$, which is desir-
able to reduce the BCS resistance. Godeke notes however
that above 24.5 atm%Sn the alloy will undergo a sponta-
neous lattice distortion at low temperatures which can lead
to strain and, Godeke suggests, reduced RF performance
[10]. Godeke recommends alloying close to 24.5 atm%Sn
but below it, which would mean that the coating produced
by the Cornell furnace is right in the desired composition
range. Unfortunately, Godeke points out, there is no infor-
mation available on the variation of $H_{c1}$ with com-
position.

X-ray photoelectron spectroscopy has a much shallower
scan depth than EDX, on the order of 10 nm [8]. By alter-
atively performing an XPS scan and sputtering the sam-
ple with Ar⁺ ions, the variation in composition with depth
could be studied. The results in Figure 7 show that the
Nb₃Sn layer has approximately uniform composition up to
a depth of \( \sim 1.5 \, \mu m \). The first surface scan is not shown as it showed foreign elements, likely from handling outside the clean room. The composition is normalized to the scan after the first etch, as differential sputtering rates give the absolute composition very large uncertainty.

Figure 7: Alternately sputtering sample and performing XPS scans shows composition versus depth.

To better characterize the Nb$_3$Sn layer, its superconducting properties were measured. The critical temperature of superconductors is often measured by induction [5], using coupled coils on either side of the sample to determine the temperature at which the sample expels magnetic flux due to the Meissner effect. An apparatus is currently being manufactured at Cornell to perform this measurement. Fortunately, while it is being fabricated, an apparatus was available to perform a simple 4-wire measurement of the transition. It involves passing a low-frequency AC current through the sample and measuring the induced voltage with a lock-in amplifier while varying the temperature of the sample. The 4-wire measurement has the disadvantage of generally measuring only the highest $T_c$ path between the leads, but it is a good early characterization to make. The measured transition is shown in Figure 8. A large discontinuity in resistance indicating a superconducting transition occurs at 18.1\( \pm \)0.2 K. This is very close to the highest recorded value for Nb$_3$Sn, 18.3 K [9]. No discontinuity is observed at any other temperature, indicating that a complete path is available between the leads with this critical temperature. The non-zero resistance below the transition at 18.1 K may result from not having the correct reference phase on the lock-in amplifier to remove any reactive components of the impedance.

Figure 8: 4-wire measurement of the Nb$_3$Sn sample indicates a critical temperature of $\sim 18.1$ K

In the same 4-wire measurement, an estimate was made of the RRR degradation in the Nb substrate resulting from the coating process. During the coating process, the valves to the pumps are closed when the furnace temperature is above 200°C, potentially allowing residual gases to reduce the RRR of the substrate, which was initially 280. To check for this, the resistance of the sample was monitored from the transition up to room temperature, as plotted in Figure 9. RRR is defined as the ratio of the 300 K resistance to the normal 4.2 K resistance. The normal resistance at 4.2 K could not be measured, but a lower bound for the RRR of 210 could be obtained using the resistance just above the transition. This shows that the RRR degradation during coating is minimal.

Figure 9: Resistance of sample versus temperature shows that minimal RRR degradation occurred during coating process.
RF TESTING OF NB$_3$SN COATINGS

A Nb bottom plate for the Cornell TE pillbox cavity was coated with Nb$_3$Sn so that RF tests could be performed. Images before and after coating are shown in Figure 10. It was also made from RRR 280 Nb and it received a 130 um BCP and HPR before coating. A 1-day degas was performed before high temperature treatment to ensure minimal RRR degradation. A small witness sample was coated with the bottom plate, which showed a composition of 23.6±0.5 atm%Sn under EDX analysis (though its tin content is likely somewhat smaller than that of the bottom plate, which was closer to the tin source), and turned pink-purple when anodized. These tests demonstrate the reliability of the coating process to produce Nb$_3$Sn of the desired composition.

Figure 10: Pictures of pillbox cavity bottom plate before (left) and after (right) Nb$_3$Sn coating.

RF testing in the pillbox cavity, models of which can be seen in Figure 11, will begin as soon as commissioning of the cavity is complete. A small T-map has also been developed for precise measurement of the small surface resistances expected from Nb$_3$Sn. See [11] for details.

Figure 11: CAD (left) and CST (right) models of the Cornell TE Pillbox Cavity.

CONCLUSIONS

Very promising results have been obtained on the first samples produced by the Nb$_3$Sn program at Cornell. $T_c$ measurements, EDX, and anodization all suggest that the desired composition has been achieved. The next step will be RF testing in a TE pillbox cavity. Fabrication of a full single-cell cavity is planned for 2012. Full-cavity T-mapping will be employed during testing to identify spots with reduced RF performance, and any spots showing lower performance will be cut out of the cavity to identify coating defects and find a way to remedy them.

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REFERENCES

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