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STUDY AND IMPROVEMENT OF LIQUID TIN DIFFUSION PROCESS TO SYNTHESIZE Nb_3Sn CYLINDRICAL TARGETS*

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Abstract

Nb_3Sn films deposited on copper cavities offer significant advantages compared to conventional niobium cavities, particularly regarding the superior thermal conductivity of copper compared to niobium. The enhanced heat exchange provided by copper enables the utilization of cryocoolers, thereby reducing cryogenic costs and minimizing the risk of thermal quench. Coating substrates with complex geometries via DC Magnetron Sputtering, such as elliptical cavities, may necessitate non-planar-shaped targets, which are challenging to produce using traditional powder sintering techniques. The LTD technique, previously developed at LNL for SRF applications, allows the deposition of thick and uniform Nb_3Sn coatings onto Nb substrates, even those with complex geometries. This work presents advancements in the LTD process and improvements in the experimental setup, in order to avoid Cr contaminations previously reported.

INTRODUCTION

Thin film deposition of Nb_3Sn is promising for superconducting radio frequency (SRF) applications, offering higher critical temperature and theoretical accelerating gradient compared to Nb. Nb_3Sn thin films on Nb bulk cavities achieved excellent performance via Vapor Tin Diffusion (VTD). However, there is strong interest in using PVD techniques to grow Nb_3Sn on a Cu substrate due to its higher thermal conductivity [1].

Conventional sintering from powders faces challenges in implementing the required features for cooling the cylindrical cathode due to material fragility. An alternative approach involves producing targets through the growth of thick films of Nb_3Sn directly on a niobium substrate using the Liquid Tin Diffusion (LTD) technique.

Previous work done at LNL showed the feasibility of LTD technique, that allowed the growth of thick layer of Nb_3Sn, even on complex geometries [2]. However, a significant limitation arose from Cr contamination in the samples caused by the Inconel chamber.

Between 2022 and 2023, further experimentation was conducted using the same chamber to enhance the process and achieve increased thickness. Subsequently, in 2023, a complete redesign of the system was implemented to mitigate contamination issues [3].

EXPERIMENTALS

Nb_3Sn is synthesized directly on a bulk Nb 1" circular target by direct immersion in liquid tin (see Fig. 1).

Sample Preparation

The circular target samples are obtained from an RRR300 niobium plate and cut using water jet cutting. The unique shape of the samples is specifically designed to be hung from the niobium wire of the manipulator using a hook, and a protrusion is added on the lower part to prevent the formation of niobium droplets. Both the hook and the lower protrusion are subsequently cut for proper mounting of the target on the magnetron.

The niobium substrates undergo ultrasonic cleaning and subsequent Buffer Chemical Polishing (BCP) using a mixture of HF, HNO_3, and H_3PO_4 in a 1:1:2 ratio for a duration of five to ten minutes. To facilitate pre-nucleation, the substrates are then anodized at 20 V for one minute in a NaOH solution, resulting in the formation of a 70 nm Nb_2O_3 layer.

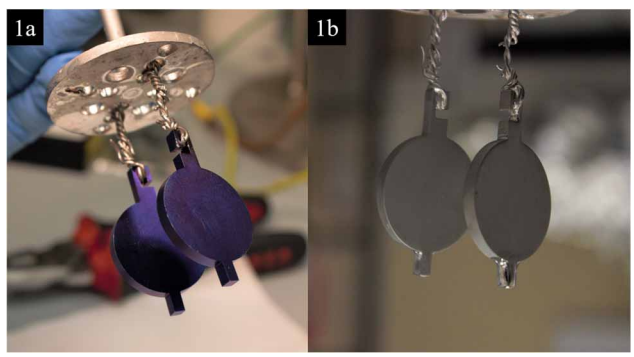

Figure 1: Nb 1" circular targets mounted on the sample holder before (a) and after (b) dipping process. The blue colour (a) is due to the anodization process.

The whole process involves the use of two separate UHV systems:

LTD System

The Liquid Tin Diffusion (LTD) system consists of an Inconel chamber as the main component, along with an ultra-high vacuum pumping system, a linear manipulator, a tin-containing crucible furnace, a sample annealing furnace, and a water jacket. The samples are securely fixed to the manipulator using niobium wires. The system is heated and evacuated to achieve a base pressure of 10^{-8} mbar.

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The process proceeds as follows:

1. *Ramping:* The lower furnace is activated to degas the crucible, followed by the activation of the upper furnace after an hour.
2. *Nucleation:* The substrates are placed in the annealing zone at the centre of the chamber and maintained at a temperature of 600 °C for 3 to 9 hours.
3. *Coating:* The temperature of the system is increased to 1000 °C using the upper furnace and maintained for 2 to 15 hours.
4. *Dipping:* The substrates are immersed in the liquid tin crucible at 1000 °C for a duration of 5 to 48 hours using the manipulator.
5. *Vapour Annealing:* The samples are brought back to the centre of the chamber and heated at 1000 °C in the presence of tin vapours from the crucible for a period ranging from 5 to 36 hours.
6. *Annealing:* The lower furnace is gradually cooled to prevent tin deposition on the sample surface, allowing annealing for 20 to 48 hours. The upper furnace is maintained at a temperature near 1000 °C.
7. *Cooling:* The samples are moved to the upper region of the water jacket to fix the phase.

Sputtering System

The DC Magnetron Sputtering system comprises an ultra-high vacuum pumping system, a 1-inch magnetron for the target obtained via the LTD method, and a heated sample holder. The system is heated to 750 °C and evacuated to a base pressure of 10^{-6} mbar. Post-process annealing can be performed to enhance the A15 phase of the deposited film.

RESULT AND DISCUSSION

In this study, we aimed to investigate the possibility of a diffusion saturation point of Nb_3Sn into Nb and the ability to modulate tin content by varying the vapour annealing step. To achieve this, a series of tests were conducted using the previous system with the Inconel vacuum chamber. Regarding the diffusion saturation, the most significant test conducted was the T4 process, and the corresponding process values are presented in Table 1.

Table 1: Process T4 Parameters

Process time (h)	Upper Furnace T(°C)	Lower Furnace T(°C)	Step
2	600	1000	Nucleation
2	1000	1000	Vapour
38	1000	1000	Dipping
32	1000	1000	Annealing w. Vapours
32	1000	1000	Annealing

In this process, the dipping time was extended up to 38 hours, keeping low pre-nucleation and vapour nucleation times. The samples were prepared as previously described.

Micrographs obtained through SEM analysis of the central region of the target reveal the presence of crystalline formations on the surface, ranging in size from 2 to 10 µm (Fig. 2a). The backscattered electron detector highlights the significant chromium contamination on the surface, manifesting as dendritic structures in certain areas of the sample (Fig. 2b). EDS analysis confirms the presence of chromium, iron and nickel contaminations and indicates a non-stoichiometric composition of Nb-Sn, that resulted 85% Nb and 15% Sn (Atomic %), with a 5:1 ratio.

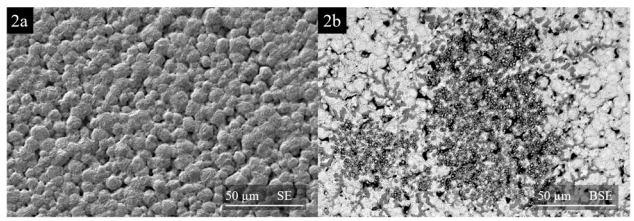

Figure 2: SEM micrographs of the target's surface taken with secondary electron detector (a) and backscattered electrons detector (b).

A section of the target was analysed to assess its characteristics. SEM analysis reveals that the thickness of the Nb_3Sn layer measures approximately 80 µm (Fig. 3). The observed thickness of Nb3Sn follows Fick's law of diffusion with excellent approximation, showing no sign of saturation down to 80 µm (Fig. 4).

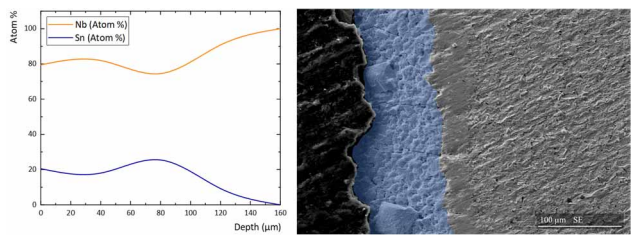

Figure 3: EDS area analysis in increasing sample depth of the target's section with SEM micrograph for assessing the thickness. Highlighted in light blue the Nb_3Sn layer.

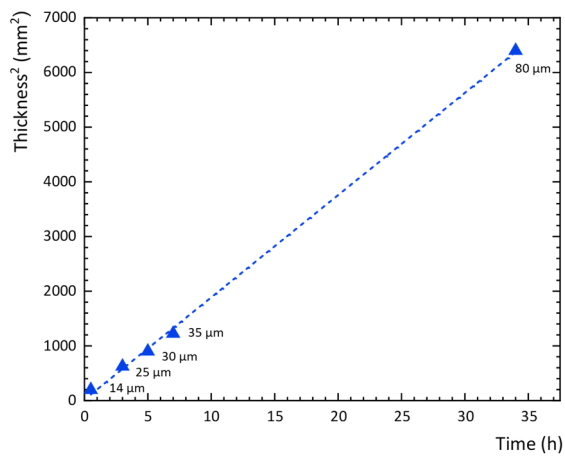

Figure 4: The graph illustrates how the experimental data from the dipping processes closely follows the Fick's law of diffusion (dashed line).

From the previous test data, combined with three new tests conducted to study tin modulation, it was observed

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that the annealing phase with vapours plays a crucial role in determining the final tin concentration on the target. This phenomenon is attributed to the presence of tin vapours and the high substrate temperature during this phase.

NEW SYSTEM DESIGN

In order to avoid Cr contamination, a new bulk Nb chamber has been already manufactured. To prevent premature oxidation of the niobium chamber at the high temperatures it will be exposed to, a new high-vacuum chamber has been designed and commissioned. The new chamber features a front-opening door for inspection and multiple CF flanges to allow for enhanced flexibility and future upgrades capability. The chamber is designed to be fully water-cooled and will be mounted on a mobile and modular system to facilitate its usage (Fig. 5).

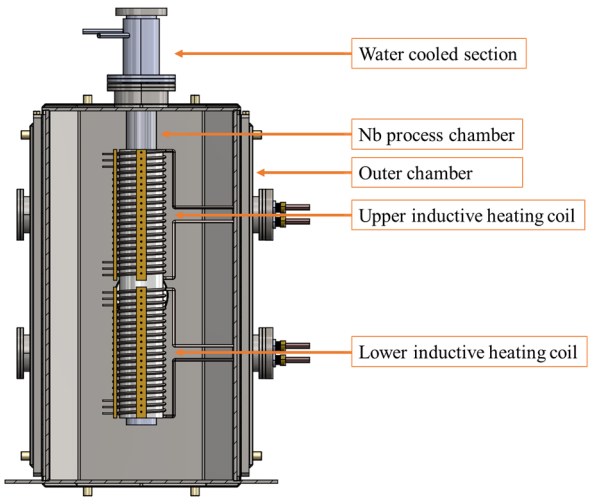

Figure 5: Drawing section of the Nb process chamber inside the containment HV chamber.

Regarding the heating process, a new custom-made induction heating system has been designed and implemented. This system enables complete control of the process parameters via a computer interface, including the option for remote control and monitoring. The induction heating system has been configured to address the specific requirements of heating two distinct zones within the chamber independently, ensuring the execution of various process steps. Simulations have been conducted to size and optimize the induction heating system. Power levels of 1800W and 1700W have been selected for the upper and lower coils, respectively. Each inductor consists of 20 turns.

Table 2: Heating System Simulation Parameters with Both Inductors Active

Process time (h)	Upper Furnace T(°C)
Power to Nb	2638 W
Inductors losses	862 W
Efficiency	75.3 %
I1 (RMS)	151.6 A
I2 (RMS)	144.4 A

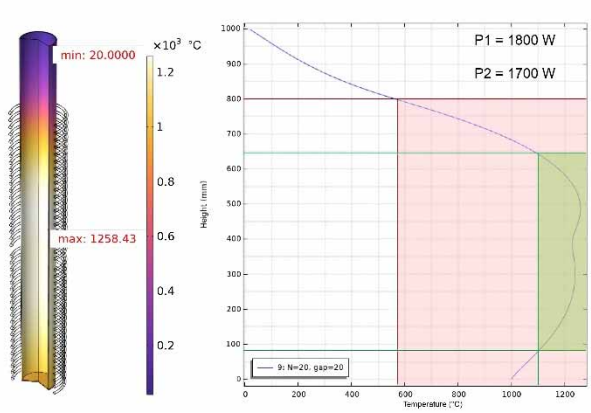

Figure 6: Temperature distribution simulation on the Nb chamber with both inductors running at maximum power.

Table 3: Heating System Simulation Parameters of the Upper Coil Active

Process time (h)	Upper Furnace T(°C)
Power to Nb	1463.5 W
Inductors losses	563.5 W
Efficiency	73.2 %
I1 (RMS)	167 A

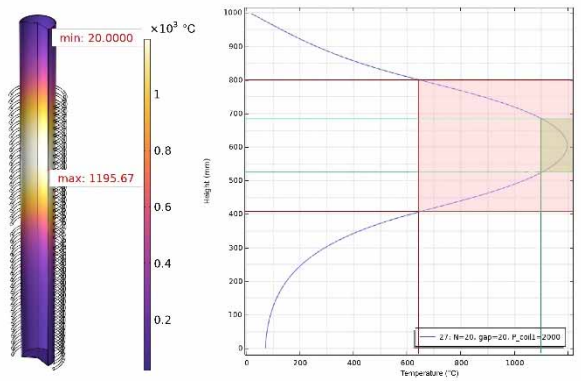

Figure 7: Temperature distribution simulation on the Nb chamber with just the upper coil active at maximum power.

Figure 6 illustrates the maximum achievable temperature of the system, exceeding 1200 °C at full power for both inductors, with a coverage of about 70% of the chamber at 1000 °C. Figure 7 shows the maximum temperature achievable by the upper inductor alone, surpassing 1100 °C. Complete parameter details for both simulations are provided in Table 2 and Table 3. This configuration ensures the attainment of selective heating in two different zones of the chamber.

CONCLUSION

The absence of a diffusion saturation point for Nb_3Sn in Nb has been demonstrated, making the process applicable even for very thick layers of Nb_3Sn on the Nb target substrate. This allows for prolonged use of sputtering targets without the need for repeated dipping processes. A significant finding is the ability to modulate the tin concentration

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through the annealing step with vapours, enabling future studies on achieving the appropriate concentration to produce stoichiometric Nb3Sn films. The newly designed and commissioned system will effectively overcome the main issue encountered in the past, which is chromium contamination.

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