

Optimization of Superconducting Nb₃Sn Electrochemical Film Technologies

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An electro-chemical deposition technique, under US Patent Application, to produce Nb₃Sn coatings was developed in the last few years by FNAL in collaboration with Politecnico di Milano. In this summary report of my training period I describe how to realize superconducting Nb₃Sn thin films through electro-deposition processes onto a Nb substrate followed by heat treatments. SEM and EDS analysis are performed in order to characterize the cross section of the samples during the fabrication. The phase diagram critical current against magnetic field of the samples is eventually measured. Optimizations of the process are made in order to improve the superconducting properties of the samples. Future research and applications are also presented. Details on my contributions to the project are given in the conclusions.

Nb₃Sn PROPERTIES

Nb₃Sn is an intermetallic compound of niobium and tin having an A15 crystal structure. It has a critical temperature of 18.3K and withstands magnetic fields up to 30T. Indeed, Nb₃Sn is largely diffused for applications where high critical currents are required, e.g. magnets with DC persistent fields larger than 10T. Nevertheless, it is extremely brittle and its critical current is strain sensitive, meaning that high stresses on the sample may reduce or totally destroy the alloy superconductivity.

The Nb₃Sn phase is produced through three DC electro-plating steps onto a Nb substrate followed by heat treatment in inert atmosphere.

ELECTRO-PLATING

Electroplating is a process for applying a metallic coating on a metal surface by electro-deposition from a suitable electrolyte solution. The object to be plated is connected as cathode in the electrolyte solution and, when the current is applied, positively charged ions of the anode will be discharged and deposited as a film on the cathode. The solutions for the electroplating steps are obtained through mixing processes by using the hotplate Corning PC-620D. The electro-deposition processes are done using the Legor SixStation plating system. The temperature is controlled by a heater and the solution can be agitated with a magnetic stirrer. In heating processes it is important to use only pyrex beakers, since they can sustain high temperatures without breaking.

Step 1: Cu seed layer onto the Nb substrate

The composition of the bath is the following:

- HCl: 67.8ml
- H₂SO₄: 217.4ml
- CuSO₄: 120g

- H₂O: as needed to achieve 2L

The HCl allows to raise the acid concentration in the solution.

The bath has to be made adding first 600ml of distilled water, followed by liquids and salts slowly and in the same order as listed above. It is not necessary to heat the mixing solution. A magnetic stirrer has to be inserted, with a velocity around 260rpm or more.

For the electro-plating process, the anode is the pure Cu electrode and the cathode is a Nb substrate. The temperature of the bath is around 40°C. Prior to the deposition, the substrate is immersed for 1min in 49% hydrofluoric acid. Then both electrodes are cleaned with sandpaper and acetone in order to reduce the presence of oxides on the surface. Indeed, oxides could reduce the adhesion of electro-deposited metals and act as a diffusional barrier layer during the heat treatment, hindering the formation of the superconducting phase. After the deposition the electrodes are rinsed in water.

Step 2: Sn layer onto the Cu seed layer

The composition of the bath is the following:

- Solderon Acid HC: 430ml
- Solderon Tin HS-300 Concentrate: 333ml
- Solderon MHS-W Primary: 200ml
- H₂O: as needed to achieve 2L

The Solderon MHS-Primary is necessary to maintain smooth deposits and throwing power. The Solderon Acid HC allows to raise the acid concentration in the solution. The Solderon RD Concentrate is designed to minimize the oxidation of tin in the electrolyte.

The bath has to be made adding first 600ml of distilled water, followed by liquids slowly. The order of mixing is irrelevant and is not necessary to heat the mixing solution. A magnetic stirrer has to be inserted, with a velocity around 260rpm or more.

For the electro-plating process, the anode is a pure Sn electrode and the cathode is the Nb/Cu sample. The temperature of the bath is 50°C. Prior to the deposition, the Sn layer is cleaned with sandpaper and acetone and after the deposition both electrodes are rinsed in water.

Step 3: Cu barrier layer onto Sn

The composition of the bath is the following:

- $\text{Cu}_2\text{P}_2\text{O}_7$: 52g
- NaNO_3 : 10g
- $\text{Na}_4\text{P}_2\text{O}_7$: 360g
- H_2O : as needed to achieve 2L

The copper pyrophosphate $\text{Cu}_2\text{P}_2\text{O}_7$ promotes an efficient dissolution of the anode and prevents the formation of insoluble salts. The sodium nitrate NaNO_3 and the sodium pyrophosphate $\text{Na}_4\text{P}_2\text{O}_7$ are added to improve the deposition rate and the smoothness of the coating.

The bath has to be made adding first 600ml of distilled water, followed by liquids and salts very slowly while heating up to 100°C at least. A magnetic stirrer has to be inserted, with a velocity around 1000rpm or more. It is also recommended to agitate manually the bath in order to speed up the mixing process.

For the electro-plating process, the anode is a pure Cu electrode and the cathode is the Nb/Cu/Sn sample. The temperature of the bath is 50°C. Prior to the deposition, the Cu layer is cleaned with sandpaper and acetone and after the deposition both electrodes are rinsed in water.

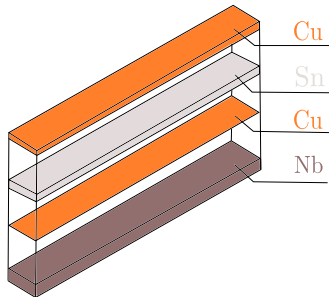


FIG. 1: Layers deposited onto the substrate during the three electro-deposition steps. For simplicity, this scheme shows only the upper surface of the sample but of course the whole immersed surface of the sample is plated.

Laws and Parameters of Electrolysis

The weight W of substance released/deposited during an electro-plating process can be computed using the Faraday law:

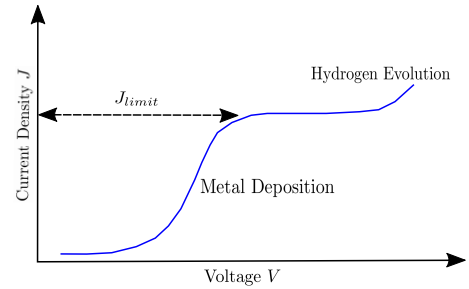


FIG. 2: Tafel plot showing the current density against voltage in a plating cell (the current density axis is logarithmic). J_{lim} is the limiting current density over which hydrogen evolution occurs.

$$W = \frac{It}{F} \cdot \frac{A}{Z}$$

where I is the electrode current, t is the time for which that current flows, A is the atomic weight of the substance, Z is the number of electrons involved in the electrode reaction (valency) and F is the Faraday constant ($1F = 96.500\text{Cmol}^{-1}$). The weight of the plating on the cathode is thus a linear function of the total electric charge passed through the substance, i.e. It . Moreover, the average thickness deposited will also depend on the density of the material.

The rate of the electrochemical reaction is related to the overpotential by the Tafel equation. On a single electrode it reads:

$$\eta = A \cdot \log \left(\frac{J}{J_0} \right)$$

where η is the overpotential, A is the Tafel slope, J is the current density and J_0 is the exchange current density i.e. the current at zero overpotential. In Fig.(2) it is shown the current density against the voltage in a plating cell. Since the metal ions cannot be deposited faster than the time they spend to arrive at the cathode surface, there is a limiting current density J_{lim} , which of course depends on the plating parameters. If the applied voltage is increased beyond that limit, other reactions will start to occur, such as the evolution of hydrogen.

The surface morphology of the deposited layers depends on various parameters. In [4] the effect of those parameters are investigated and it turns out that:

- As the DC current density increases:
 - The nucleation rate increases, resulting in a reduction in the grain size.
 - The flow rate of ions toward cathode becomes higher with respect to the replenishment of the ions from the anode. Thus a gradient is

created around solution/cathode interface and the deposition takes place at certain protrusions/nucleation sites on the sharp boundaries of the cathode, whose density increases with the current density. The smaller the number of protrusions the faster will be their growth. This results in the development of an unstable growth front, giving dendritic structures in a random orientation. Then the DC current flows more densely on the sharp boundaries than to the flat bulk of the sample, which implies a non uniform current distribution.

- The adhesion between layers decreases.
- As the deposition time increases, the amount of coated metal increases.
- As temperature increases:
 - The grain size increases.
 - The conductivity of the electrolyte solution decreases, due to the decomposition of chemical species at higher temperatures.
- As the PH of the solution increases the porosity and the roughness of the deposits increases.
- As the stirring rate increases the concentration of ions coming out from the anode gets more distributed in the electrolyte, then:
 - The porosity and the roughness of the deposits decreases.
 - The grain size increases.
 - The deposition rate decreases.

On the other hand, a too large stirring rate causes the ions to reach the electrode surface at a faster speed, resulting in a reduction of the deposition rate.

Thus, in order to improve the uniformity and the adhesion of the depositions, it is more convenient to use a pulsed power generator. The pulsed waveform is characterized by various time and current parameters, which are shown in Fig.(3). The period T of the waveform is given by $T = t_F + t_R$ and the frequency f is its inverse. The duty cycles for the forward and reverse on times are defined as:

$$\gamma_F = \frac{t_{F,on}}{T} \quad \gamma_R = \frac{t_{R,on}}{T}$$

and the average current is given by:

$$\langle i \rangle = i_{F,on}\gamma_F + i_{R,on}\gamma_R$$

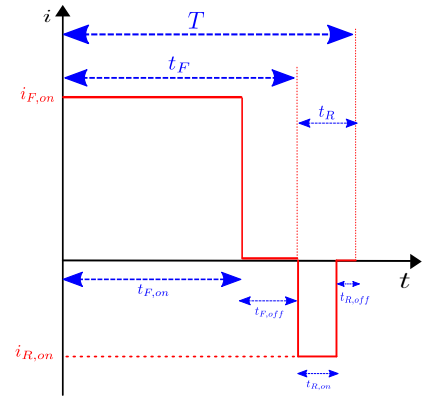


FIG. 3: Parameters pulsed waveform: forward duration t_F , forward-on time $t_{F,on}$, forward-off time $t_{F,off}$, reverse duration t_R , reverse-on time $t_{R,on}$, reverse-off time $t_{R,off}$, forward-on current $i_{F,on}$, reverse-on current $i_{R,on}$.

During $t_{F,off}$, $t_{R,on}$, $t_{R,off}$ ions migrate away from the cathode surface and this reduces the amount of nucleation sites, implying a more uniform coating.

Clearly the space of parameters becomes much larger than in the DC case. In [4] the effects of these new parameters are described and it turns out that:

- As the frequency increases the pulse duration is higher. This means that less time is available for the charging and discharging of the electrode during on/off times and this implies that:
 - The nucleation rate increases with a limited growth rate, resulting in a dense microstructure.
 - The average roughness and thickness of the film decreases.
- As the forward duty cycle increases:
 - The grain size of the deposits decreases continuously, because of larger overpotential at a longer current on times.
 - The porosity and the roughness of the deposits increases due to the increase in average current flow time.

Finally the cell geometry and the position of the electrodes affects the thickness of the deposited layer. Because both electrodes are good conductors, it can be assumed that the potential between them is the same everywhere. As a result, the current density at any specific local area of the electrode is a function of the distance to the opposite electrode. In Fig.(4) are shown few examples. In order to have a uniform deposition on both sides of the sample, a choice could be to put the cathode perpendicular to the anode and to the stirrer flux lines, as it is shown in Fig.(5).

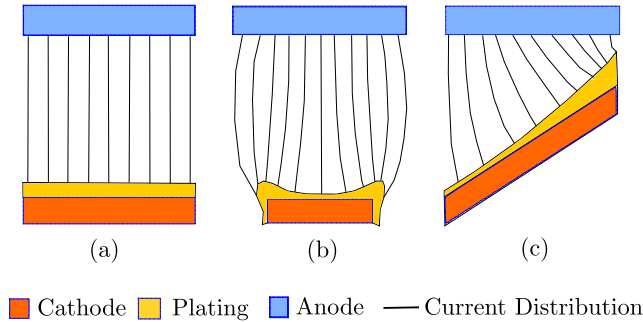


FIG. 4: Examples of current distribution and thickness deposited layer for three different orientations of anode and cathode. The shape of both electrodes and their relative orientation affect strongly the characteristics of the deposition.

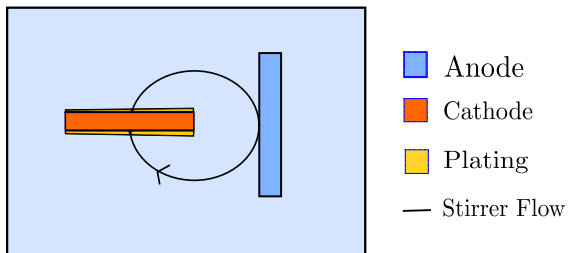


FIG. 5: Perpendicular disposition of the electrodes. The plane of the cathode is perpendicular to the plane of the anode and to the flux lines induced by the stirrer.

HEAT TREATMENT

The phase diagram of Nb-Sn is shown in Fig.(6). In the binary system Nb-Sn, the single-phase Nb_3Sn is formed only above $930^\circ C$ between 18% and 25% of Sn. At temperatures below $845^\circ C$ the two non superconducting phases $NbSn_2$ and Nb_6Sn_5 are also stable and they grow at the interface, together with the Nb_3Sn phase. Thus, in order to minimize the formation of undesired low- T_c phases, it would be necessary to reach a reaction temperature above $930^\circ C$. Notice that if the Sn concentration is below 25% the Nb_3Sn phase remains the only thermodynamically stable phase during cool down to room temperature.

However, in the ternary system Nb-Cu-Sn, the phase Nb_3Sn is the only stable phase even at lower temperatures due to the addition of Cu. Additionally, the presence of Cu does not dramatically change the superconducting behaviour of the material. This is why before depositing Sn there should be a Cu seed layer onto the Nb substrate.

Thus, the Nb/Cu/Sn/Cu samples undergo the heat treatment shown in Fig.(7).

- The initial step is at $T_1 \approx 206^\circ C$ for $t_1 = 72h$. T_1 is slightly lower the Sn melting point to allow the relaxation of the internal stresses in the metal

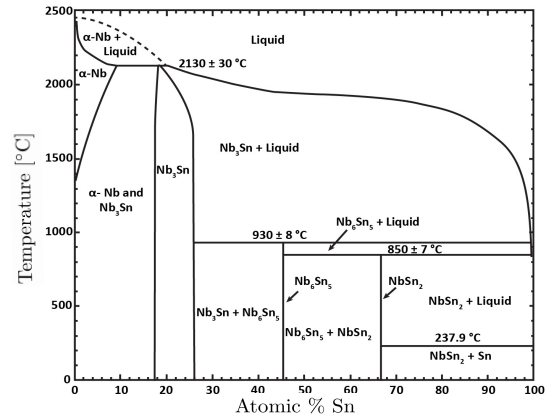


FIG. 6: Phase diagram of Nb - Sn.

layers and to start the diffusion between Cu and Sn.

- The second step is at $T_2 \approx 456^\circ C$ for $t_2 = 10h$. This step allows the formation of a liquid tin phase and make start the diffusion with Nb and Cu. After this step, an external bronze ϵ phase and a most internal η phase are formed.
- The third step is at $T_3 \approx 700^\circ C$ for $t_2 = 24h$. After this step, the Nb_3Sn superconducting phase is formed.

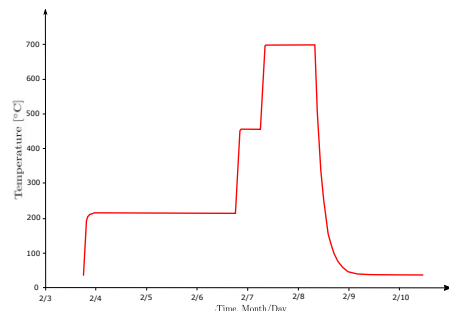


FIG. 7: Heat treatment of Nb/Cu/Sn/Cu samples.

The heat treatment is performed using a computer controlled tubular furnace. The oven is $1m$ long and has three different induction resistances, one at the centre and two on the sides, that can be separately programmed to maintain the temperature gradient the most possible low. The furnace is provided of valves for the connection to vacuum pumps and a gas tank. The sample is put on an inox sample holder, and placed at the centre of the heating chamber. Before the heat treatment, vacuum is generated in the retort and argon is later inflated and let flow, always maintaining a small internal overpressure to avoid air entrance. At the end of the cycle the oven is turned off, and the sample is removed when the internal temperature is lowered enough.

STOICHIOMETRIC CALCULATION

It is possible to do a stoichiometric calculation to make previsions on the thickness of the Nb_3Sn film after the heat treatment.

The Nb belongs to the space group number 229 and it has an fcc structure (2 atoms per unit cell) with the following cell parameters:

$$\begin{aligned} a &= 3.004\text{\AA} & b &= 3.004\text{\AA} & c &= 3.004\text{\AA} \\ \alpha &= 90^\circ & \beta &= 90^\circ & \gamma &= 90^\circ \end{aligned}$$

The Sn belongs to the space group number 141 and it has an tetragonal structure (1 atom per unit cell) with the following cell parameters:

$$\begin{aligned} a &= 5.8318\text{\AA} & b &= 5.8318\text{\AA} & c &= 3.1819\text{\AA} \\ \alpha &= 90^\circ & \beta &= 90^\circ & \gamma &= 90^\circ \end{aligned}$$

Assume an uniform deposition of the first two layers of Cu and Sn and let t_{Cu} and t_{Sn} be as the thickness of Cu layer and Sn layer respectively.

Let V_{sub} the volume of the substrate and let V_1 and V_2 be the volume of the sample after respectively the first and the second electro-deposition step. Then:

$$\begin{aligned} V_{sub} &= l_{sub}w_{sub}t_{sub} \\ V_1 &= (l_{sub} + t_{Cu})(w_{sub} + t_{Cu})(t_{sub} + t_{Cu}) \\ V_2 &= (l_{sub} + t_{Cu} + t_{Sn})(w_{sub} + t_{Cu} + t_{Sn})(t_{sub} + t_{Cu} + t_{Sn}) \end{aligned}$$

The number N_{Nb} of Nb atoms in the substrate and the number N_{Sn} of Sn atoms in the thin layer are respectively given by:

$$N_{Nb} = 2 \frac{V_{sub}}{V_{Nb,cell}} \quad N_{Sn} = \frac{V_2 - V_1}{V_{Sn,cell}}$$

In order to realize the Nb_3Sn phase, the following inequality must hold:

$$N_{Sn} \leq \frac{1}{3}N_{Nb}$$

which implies:

$$V_2 - V_1 \leq \frac{2}{3} \frac{V_{Sn,cell}}{V_{Nb,cell}} V_{sub}$$

from which it is possible to find out the maximum value of t_{Sn} .

According to [1], the optimized values of the thickness for each layer should be:

- First layer: $1\mu\text{m}$
- Second layer: $15\mu\text{m}$

- Third layer: $15\mu\text{m}$

Indeed, the thickness of the Cu seed layer should be approximately the 10%-15% of the expected Nb_3Sn phase formed, which should be around $10\mu\text{m}$. Thus a Cu seed layer of $2\mu\text{m}$ should be sufficient to have a good diffusion with Sn.

SEM AND EDS ANALYSIS

The cross section and the surface topography of the sample can be studied using the Scanning Electron Microscope (SEM), whereas the composition of the coating can be determined by Electron Dispersive Spectroscopy (EDS). The cross sections of interest are:

- Transversal cross section of the sample before the heat treatment, in order to find the thickness of each electro-deposited layer.
- Longitudinal cross section of the sample after the heat treatment, in order to find the thickness of the Nb_3Sn phase formed.

Preparation of the sample

Before using the SEM, the sample has to be prepared properly in order to fulfil the dimensions required by SEM and to expose a minimum distorted cross section. Thus, the sample has to be cut and this causes deformations of the order of $10 \div 100\mu\text{m}$ on the cut boundary. For next steps, it is useful to hold the sample in vertical position by using a clip, like it is shown in Fig.(8).

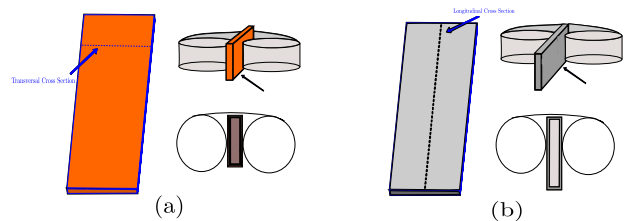


FIG. 8: (a) Cut of the sample to look at the transversal cross section before the heat treatment. (b) Cut of the sample to look at the longitudinal cross section after the heat treatment.

Then the sample undergoes an epoxy process. The resin has to be conductive, otherwise there would be charge localization on the surface of the sample during the SEM technique, producing a brighter image. The mold is realized putting the sample hold by the clip and 30g of the bakelite KounductoMet inside the chamber of the SimpliMet 300 mounting press, which is set with the following parameters:

- Heat time: 1min

- Cool time: $3min$
- Pressure: $4200psi$
- Temperature: $300F$

Both pressure and heating are gradually applied.

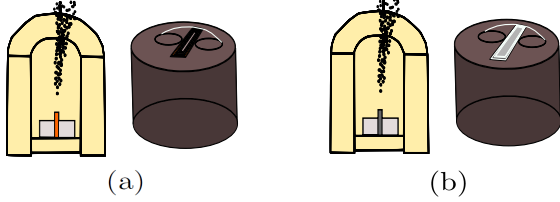


FIG. 9: (a) Mounting press setup and mold to look at the transversal cross section before the heat treatment; (b) Mounting press setup and mold to look at the longitudinal cross section after the heat treatment.

One possibility for looking at the longitudinal cross section of the sample would be to cut the mold obtained after this epoxy process with the help of a Buehler Isomet low speed saw.

Then a grinding process has to be made for the front size of the mold in order to produce a smooth and flat surface. The surface of the grinder is made by hard particles, whose size characterizes the level of grit of the surface. It is better to do a wet grinding with distilled water, in order to wash away the removed material of the sample, as long as the sample is not sensitive to water. This is very important, especially for high level of grit.

With the help of a Buheeler HandiMet roll grinder it is possible to perform grinding with 320, 400 and 600 grit. At fixed level of grit, the sample has to be periodically dragged along the grinder surface (5 times are sufficient) and rotated (preferably of 45°) in order to do not have a tilted surface. For this purpose it may help labelling the back side of the mold in order to identify the different orientations. The general prescription is to move from one grit value to the successive one only if there are no scratches left over from the previous step, which can be checked using an optical microscope. The first grit level has to be kept until the whole cross section of the sample becomes clearly visible.

Further level of grits, like 800 and 1200, can be made using the Metprep 1 grinder/polisher. During this phase it is not necessary to rotate the sample, since it is very unlikely to realize a tilt of the surface. Thus, at fixed level of grit the sample has to be hold steadily to the grinding surface for $1min$. The angular velocity of the grinding surface can be set to $100rpm$. The automatic rotation has to be started once the sample touches the surface, whereas to stop the process is sufficient to take away the sample from the surface and then to stop the rotation.

Eventually the sample undergoes a polishing process. First, it is put into a fixer which allow to have a completely flat surface independently from tilts of the sample surface (clearly the height of the sample must be higher than the height of the fixer). Then the sample is inserted into a chamber filled with a liquid containing hard particles and it is kept in rotation under the vibrations of the machine. This process is more gentle than grinding and it removes material much more slowly. Indeed, hard particles are attached to flexible fibres which gently polish the sample surface. This process is made with the help of the vibrometer VibroMet 2 with rotational speed set to 60%; it may take several hours. At the end of the process, the sample has to be rinsed with acetone and then dried with a blower.

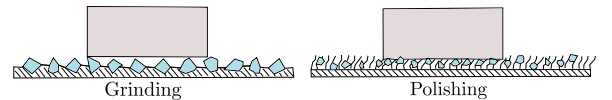


FIG. 10: Scheme of grinding and polishing processes.

After the polishing process, the scratches in the surface of the sample should be oriented along the same direction and it should be possible to see the grain boundaries. The sample is now ready to be observed with the SEM.

SUPERCONDUCTING PROPERTIES

In order to determine whether the sample is superconducting or not, tests are performed both in a field parallel and perpendicular to its surface, like it is shown in Fig.(11).

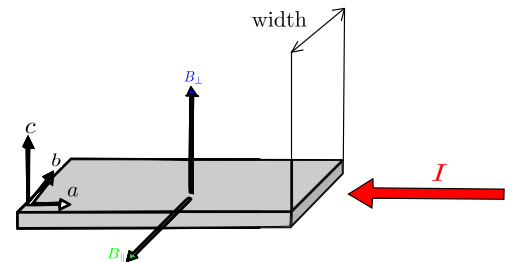


FIG. 11: Scheme of sample orientation used with respect to the magnetic field B for the superconducting test.

In [5] parametrization of the critical current are discussed. At fixed strain this parametrization reduces to the following expression [6]:

$$I_c(B, T)B = h_0 \left(\frac{B_{c2}(T)}{B_{c20}} \right)^\eta \left[1 - \frac{B}{B_{c2}(T)} \right]^2 \left(\frac{B}{B_{c2}(T)} \right)^{0.5}$$

where I_c is the critical current, B is the magnetic field, B_{c2} is the upper critical magnetic field and B_{c20} the up-

per critical magnetic field at $T = 0K$. It is possible to find B_{c20} by using the following relation:

$$\frac{B_{c2}(T)}{B_{c20}} = \left[1 - \left(\frac{T}{17.5K} \right)^{1.5} \right]$$

where h_0 , B_{c20} and η are free parameters for the fit.

In order to perform critical current measurements, the sample is held at the bottom of a probe and then inserted into a magneto-cryostat, which consists primarily of a vacuum insulated helium dewar (main bath) containing a superconducting solenoid at the bottom. In order to make measurements at different temperatures, the main cryostat feeds a second smaller helium cryostat, called Variable Temperature Insert (VTI), which is inserted inside the main dewar, down into the solenoid bore. Current is supplied to the sample by pressure contact between the copper rings and two copper lugs welded on the probe. A thin layer of indium is used to improve the electrical contact between them.

SAMPLES AND RESULTS

The experimental setup used are shown in Fig.(2). Samples were realized onto substrates with a parallelepiped or disk shape, as it is shown in Fig.(12).

For the parallelepiped samples, let l , w , t be respectively the length, width and thickness of the substrate and let h be the length of the non exposed surface. The area A_p exposed to the solution is given by:

$$A_p = 2(lw + lt) + wt$$

For the disk samples, let r and t be respectively the radius and the thickness of the substrate, let h be the vertical length of non exposed surface and let θ the angle shown in Fig.(12). The area A_d exposed to the solution is given by:

$$A_d = 2r^2 \left[\pi - \theta + \left(1 - \frac{h}{r} \tan(\theta) \right) \right] + 2rt(\pi - \theta)$$

where $\theta = \arccos \left(1 - \frac{h}{r} \right)$.

Before making the various electro-deposition steps, it is important to make previsions about the area of the immersed surface. In order to do this, making a scratch on the sample can help to underline the portion that has to be immersed.

The time between the rinsing in HF and the first electro-deposition step as well as the times between the various steps should be no more than few minutes, in order to avoid the formation of oxides.

The dimensions of the cross section of the cell are $5cm$ x $5cm$. The dimensions of the anode electrodes used are:

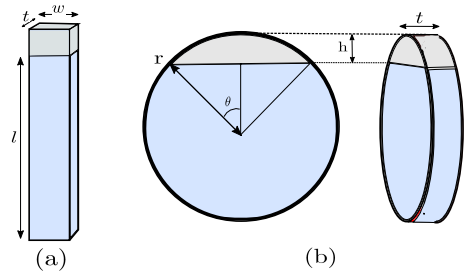


FIG. 12: (a) Samples with rectangular shape; (b) Samples with disk shape.

- Cu electrodes: $(13.0 \pm 0.5)cm$ x $(2.5 \pm 0.2)cm$ x $(0.04 \pm 0.01)cm$
- Sn electrode: $(8.5 \pm 0.5)cm$ x $(0.35 \pm 0.2)cm$ x $(0.02 \pm 0.01)cm$

The electro-deposition parameters used to realize the samples are shown in Tab.I and in Tab.II.

For all the electro-deposition step the samples are put in the middle of the cell at a distance of $(4.5 \pm 0.5)cm$ from each other. Samples from 1 to 6 were disposed with parallel orientation, whereas samples from 7 to 23 and all the disks were disposed with perpendicular orientation as it is shown in Fig.(5).

After the electro-deposition processes, the immersed surface of the sample is measured.

It comes out that a uniform deposition it is obtained with the following values of current densities respectively for steps 1, 2 and 3:

$$J_1^* = 20mA/cm^2 \quad J_2^* = 35mA/cm^2 \quad J_3^* = 15mA/cm^2$$

In Tab.II and in Tab.III there are shown the dimensions of Nb substrates and the parameters used in the various electro-deposition steps.

The first samples were realized using long deposition times in order to emphasize the effects of the parameters chosen. Once a good set of parameters was found, the electro-deposition times were reduced in order to achieve layers of few micrometers. As an example, pictures of sample 10 during the fabrication, SEM/EDS analysis and resistance as function of the temperature are shown in Fig.(13), Fig.(14), Fig.(15), Fig.(16), and Fig.(17).

In Fig.(18) it is shown the phase diagram of critical current I_C against magnetic field B obtained for the various samples produced and compared to samples produced in the last few years (denoted with "old").

In Tab.I are shown the values of B_{c20} obtained for each sample.

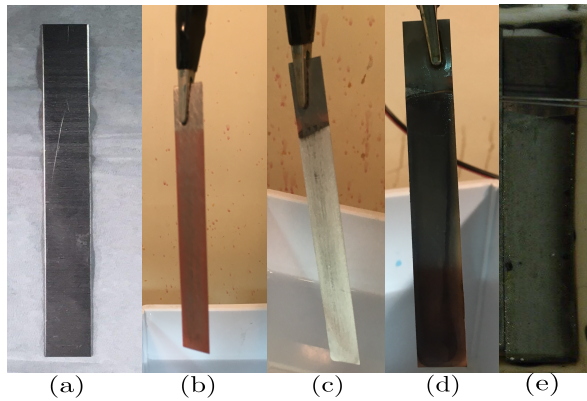


FIG. 13: Sample 10 - (a) substrate; (b) after the first electro-deposition step; (c) after the second electro-deposition step; (d) after the third electro-deposition step; (e) after the heat treatment.

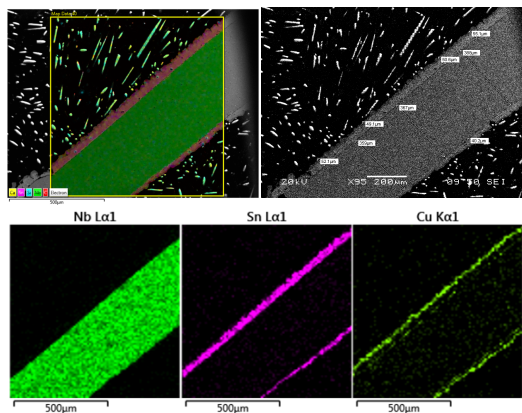


FIG. 14: Sample 10 - transversal cross section before the heat treatment. The scale is quite large but it allows to show that a quite uniform deposition for each step is formed on both sides of the sample.

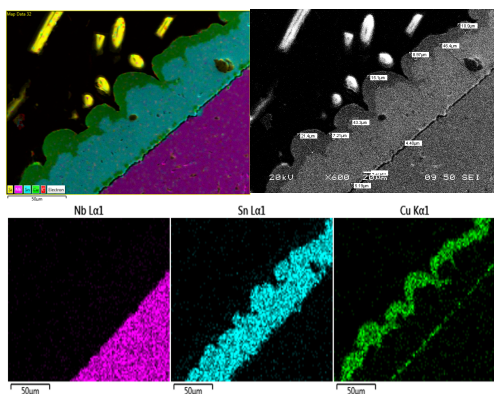


FIG. 15: Sample 10 - transversal cross section before the heat treatment (zoomed image). It is possible to estimate the thickness of each layer and therefore determine the deposition rates for each electro-plating step.

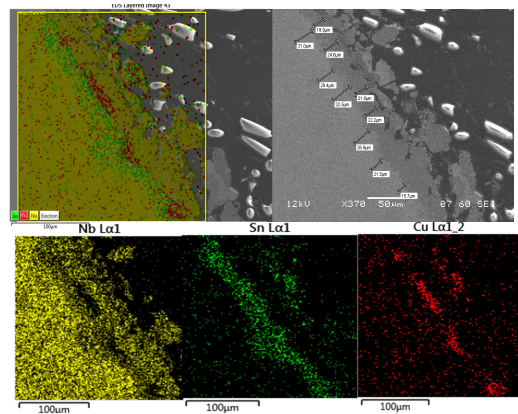


FIG. 16: Sample 10 - longitudinal cross section after the heat treatment. The superconducting phase is formed where is Sn is present. The outer layer is bronze, which is formed during the heat treatment and can be removed with appropriate etching processes.

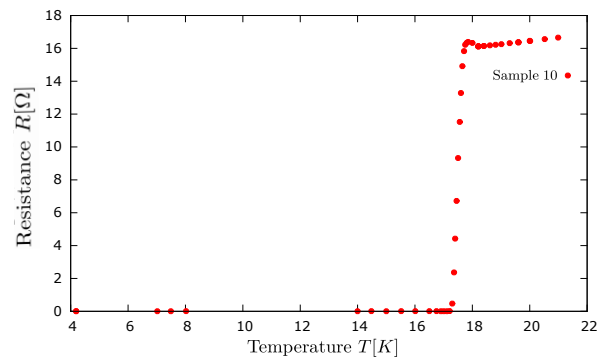


FIG. 17: Sample 10 - resistance as function of temperature. The transition is quite sharp and occurs at $T_c \approx 17.5K$.

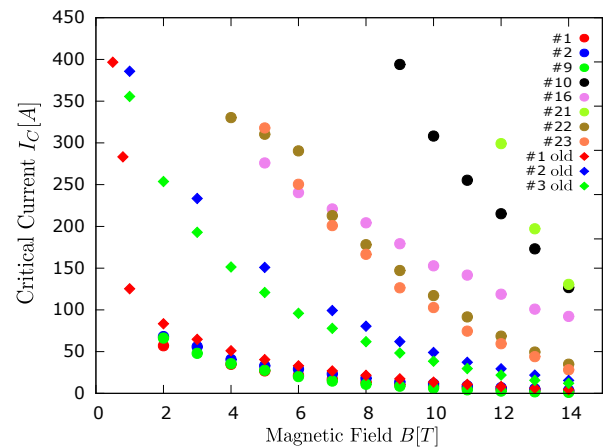


FIG. 18: Phase diagram critical current I_C against magnetic field B at $T \approx 4.2K$. The first samples produced turned out to be superconducting. Some samples got broken during the tests since the Nb_3Sn phase is very brittle. Thus, as a remark, it is convenient to realize samples with a thickness of at least $0.5mm$. Almost all the samples clearly show an improvement with respect to the old samples, indicating that the fabrication procedure was optimized.

Sample	$B_{c,20}[T]$
1	23.17
2	23.36
9	18.96
10	27.10
1 old	23.13
2 old	22.92
3 old	22.26

TABLE I: Values of B_{c20} obtained from the fits I_c against B at $T \approx 17.7K$. Data are reported without uncertainty since they are considered lower bound values.

FUTURE RESEARCH AND APPLICATIONS

The procedure can be optimized further at least in the following aspects:

- In order to improve the uniformity of the deposition on both sides of the sample, a double anode electrode could be used, as shown in Fig.(19). This requires to adjust the current applied in order to have the current densities J_1^* , J_2^* and J_3^* for the three steps.
- At fixed value of current densities, find the deposition rates by varying the times for each electro-deposition step.
- Try to optimize further the parameters for the electro-depositions.

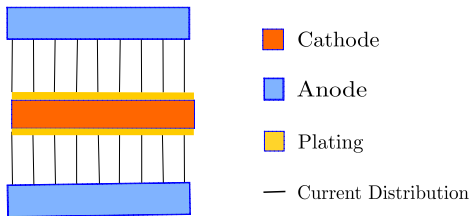


FIG. 19: Double anode configuration for the disposition of the electrodes.

Applications can be found in three main fields:

- Superconducting wires. The Nb_3Sn films could be used to research and investigate nanotechnology methods to enhance the transverse component of pinning. If a technique proves to be successful, it would be possible to work with billet manufacturing company to transfer and implement it in wires.
- Superconducting magnetic shields. Shielding capabilities depend on the total superconducting thickness of the material. For stability, each superconducting shield layer cannot be thicker than a given value. A multi-layer shield can be obtained by replicating the Cu/Sn deposition method on

sputtered Nb until the desired total thickness is achieved.

- SRF cavities (high Q, high gradient and low cost). The Nb_3Sn films could be produced onto Nb substrates of appropriate geometry (2 inch discs) for surface resistance measurements at JLab, which is related to Q. Based on results achieved, the technique could be scaled up to 3D surfaces, using the appropriate design of the anode and of customized galvanic cells as well as the appropriate software.

CONCLUSIONS

My main goal was to reproduce and optimize the original recipe. The experimental apparatus was procured and commissioned before my arrival at Fermilab, in order to synthesize thin films in-house. I was trained on:

- How to use chemicals by D.Hicks.
- How to perform the various electro-deposition steps by E.Barzi and D.Turrioni.
- How to perform grinding/polishing process and use the SEM by P.Li.

The data shown in Fig.(18), Fig.(17) and in Tab.I were collected by D.Turrioni. The first samples produced resulted already superconducting, despite the unsuccessful results in the last years in reproducing the original recipe. This allowed to make variations around the original parameters in order to optimize them. New nominal values for current densities are proposed and the result is remarkably better than the previous values, as it is shown in Fig.(18). Moreover a systematic method to realize the samples is provided in order to make the recipe reproducible. The last samples produced will be sent to Jefferson Lab and to KEK to further studies and applications.

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Parallelepiped Samples	Dimensions								Input Parameters													
	l [cm]	δ_l [cm]	w [cm]	δ_w [cm]	l [cm]	δ_l [cm]	Area[cm ²]	δ_{Area} [cm ²]	step	$V-gen$	I_{av} [A]	$\delta_{I_{av}}$ [A]	J_{av} [mA/cm ²]	$\delta_{J_{av}}$ [mA/cm ²]	time[<i>min</i>]	δ_{time} [<i>min</i>]	T [T]	δ_T [T]	f [Hz]	δ_f [Hz]	γ_F [%]	γ_R [%]
1	8.00	0.50	1.000	0.20	0.05	0.01	16.85	4.61	1	DC	0.400	0.001	23.74	6.29	75.00	0.01	40	3	-	-	-	-
									2	DC	0.700	0.001	41.54	10.96	30.00	0.01	50	3	-	-	-	-
									3	DC	0.300	0.001	17.80	4.73	90.00	0.01	50	3	-	-	-	-
2	8.00	0.50	0.93	0.20	0.05	0.01	15.77	4.53	1	DC	0.400	0.001	25.36	7.08	90.00	0.01	40	3	-	-	-	-
									2	DC	0.700	0.001	44.37	12.35	75.00	0.01	50	3	-	-	-	-
									3	DC	0.300	0.001	19.02	5.33	180.00	0.01	50	3	-	-	-	-
3	8.00	0.50	1.23	0.20	0.05	0.01	20.53	4.89	1	DC	0.400	0.001	19.49	4.44	60.00	0.01	40	3	-	-	-	-
									2	DC	0.600	0.001	29.23	6.63	60.00	0.01	50	3	-	-	-	-
									3	DC	0.350	0.001	17.05	3.89	120.00	0.01	50	3	-	-	-	-
4	8.00	0.50	1.22	0.20	0.03	0.01	20.05	4.86	1	Pulsed	0.400	0.001	19.95	4.56	60.00	0.01	40	3	50.00	0.01	50	50
									2	Pulsed	0.600	0.001	29.92	6.82	60.00	0.01	50	3	50.00	0.01	50	50
									3	Pulsed	0.300	0.001	14.96	3.44	120.00	0.01	50	3	50.00	0.01	50	50
5	8.00	0.50	1.24	0.20	0.03	0.01	20.28	4.87	1	Pulsed	0.400	0.001	19.73	4.48	75.00	0.01	40	3	50.00	0.01	70	0
									2	Pulsed	0.600	0.001	29.59	6.69	60.00	0.01	50	3	100.00	0.01	70	0
									3	Pulsed	0.350	0.001	17.26	3.92	240.00	0.01	50	3	100.00	0.01	70	0
6	8.00	0.50	1.11	0.20	0.03	0.01	18.34	4.73	1	Pulsed	0.400	0.001	21.81	5.33	75.00	0.01	40	3	50.00	0.01	80	0
									2	Pulsed	0.50	0.001	27.27	6.65	75.00	0.01	50	3	50.00	0.01	80	0
									3	Pulsed	0.50	0.001	27.27	6.65	115.00	0.01	50	3	50.00	0.01	80	0
7	8.00	0.50	1.15	0.20	0.03	0.01	18.98	4.78	1	Pulsed	0.400	0.001	21.08	5.02	3.00	0.01	40	3	50.00	0.01	70	0
									2	Pulsed	0.600	0.001	31.61	7.51	15.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	0.350	0.001	18.44	4.40	20.00	0.01	50	3	100.00	0.01	20	0
8	8.00	0.50	1.21	0.20	0.03	0.01	19.89	4.84	1	Pulsed	0.400	0.001	20.11	4.63	2.00	0.01	40	3	50.00	0.01	70	0
									2	Pulsed	0.600	0.001	30.16	6.92	12.00	0.01	50	3	50.00	0.01	10	0
									3	Pulsed	0.350	0.001	17.59	4.06	25.00	0.01	50	3	100.00	0.01	20	0
9	8.00	0.50	1.33	0.20	0.03	0.01	21.78	4.99	1	Pulsed	0.400	0.001	18.36	3.96	2.00	0.01	40	3	100.00	0.01	20	0
									2	Pulsed	0.600	0.001	27.54	5.91	12.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	0.350	0.001	16.07	3.47	25.00	0.01	50	3	100.00	0.01	20	0
10	8.00	0.50	1.40	0.20	0.03	0.01	22.95	5.07	1	Pulsed	0.400	0.001	17.43	3.62	2.00	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	0.600	0.001	26.14	5.41	15.00	0.01	50	3	100.00	0.01	20	0
									3	Pulsed	0.350	0.001	15.25	3.17	25.00	0.01	50	3	100.00	0.01	10	0
11	7.29	0.20	2.03	0.20	0.03	0.01	30.09	4.29	1	Pulsed	0.800	0.001	26.59	3.38	1.00	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	1.200	0.001	39.88	5.06	5.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	0.700	0.001	23.26	2.96	15.00	0.01	50	3	100.00	0.01	10	0
12	7.53	0.20	2.07	0.20	0.03	0.01	31.66	4.42	1	Pulsed	0.800	0.001	25.27	3.15	1.00	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	1.200	0.001	37.91	4.70	4.50	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	0.700	0.001	22.11	2.76	12.00	0.01	50	3	100.00	0.01	10	0
13	8.98	0.20	1.02	0.20	0.03	0.01	18.81	4.39	1	Pulsed	0.560	0.001	29.77	6.58	1.50	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	0.840	0.001	44.66	9.84	7.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	0.490	0.001	26.05	5.76	20.00	0.01	50	3	100.00	0.01	10	0
14	8.73	0.20	1.04	0.20	0.03	0.01	18.75	4.30	1	Pulsed	0.560	0.001	29.87	6.47	1.50	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	0.840	0.001	44.81	9.68	10.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	0.490	0.001	26.14	5.67	25.00	0.01	50	3	100.00	0.01	10	0
15	8.67	0.20	1.00	0.20	0.03	0.01	17.92	4.25	1	Pulsed	0.560	0.001	31.26	7.02	1.00	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	0.840	0.001	46.88	10.50	5.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	0.490	0.001	27.35	6.15	15.00	0.01	50	3	100.00	0.01	10	0
16	10.22	0.20	2.06	0.20	0.03	0.01	42.77	5.54	1	Pulsed	0.800	0.001	18.70	2.21	2.00	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	1.400	0.001	32.73	3.84	7.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	0.600	0.001	14.03	1.66	30.00	0.01	50	3	100.00	0.01	10	0
17	9.92	0.20	2.06	0.20	0.03	0.01	41.54	5.42	1	Pulsed	0.800	0.001	19.26	2.28	2.00	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	1.400	0.001	33.70	3.98	7.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	0.600	0.001	14.44	1.72	30.00	0.01	50	3	100.00	0.01	10	0
18	10.26	0.20	2.03	0.20	0.03	0.01	42.33	5.54	1	Pulsed	0.800	0.001	18.90	2.25	2.00	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	1.400	0.001	33.07	3.93	7.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	0.600	0.001	14.17	1.70	30.00	0.01	50	3	100.00	0.01	10	0
19	8.52	0.20	2.02	0.20	0.03	0.01	34.98	4.80	1	Pulsed	0.800	0.001	22.87	2.83	2.00	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	1.400	0.001	40.03	4.93	7.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	0.600	0.001	17.15	2.13	30.00	0.01	50	3	100.00	0.01	10	0
20	8.65	0.20	2.03	0.20	0.03	0.01	35.69	4.86	1	Pulsed	0.800	0.001	22.41	2.75	2.00	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	1.400	0.001	39.23	4.80	7.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	0.600	0.001	16.81	2.07	30.00	0.01	50	3	100.00	0.01	10	0
21	9.35	0.20	3.99	0.20	0.05	0.01	75.75	6.34	1	Pulsed	1.459	0.001	19.26	1.39	2.00	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	2.552	0.001	33.69	2.42	7.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	1.094	0.001	14.44	1.05	25.00	0.01	50	3	100.00	0.01	10	0
22	8.50	0.20	4.05	0.20	0.05	0.01	69.90	6.02	1	Pulsed	1.480	0.001	21.17	1.56	2.00	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	2.590	0.001	37.05	2.72	7.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	1.110	0.001	15.88	1.17	30.00	0.01	50	3	100.00	0.01	10	0
23	8.42	0.20	5.10	0.20	0.05	0.01	86.95	6.62	1	Pulsed	1.755	0.001	20.18	1.28	2.00	0.01	40	3	100.00	0.01	10	0
									2	Pulsed	3.000	0.001	34.50	2.18	7.00	0.01	50	3	100.00	0.01	10	0
									3	Pulsed	1.316	0.001	15.14	0.96	30.00	0.01	50	3	100.00	0.01	10	0

TABLE II: Dimensions and electro-deposition parameters of parallelepiped-shape samples produced; data in red are reasonable estimation of lost data.

Disk Samples	Dimensions								Input Parameters												
	r [cm]	δ_r																			