ISBN: 978-3-95450-233-2 ISSN: 2673-5504 doi:10.18429/JACoW-SRF2021-FROFDV06

SYNTHESIS OF Nb AND ALTERNATIVE SUPERCONDUCTING FILM TO Nb FOR SRF CAVITY AS SINGLE LAYER

R. Valizadeh[1]†, A. Hannah[1], O.B. Malyshev[1], P. Goudket[1], STFC/DL, Daresbury, Warrington, UK
G. Stenning, STFC/RAL, Didcot, UK
[1]also at Cockcroft Institute, Daresbury, Warrington, UK
D. Seal[1], D.A. Turner[1], B.-T. Singh Sian1, Lancaster University, Lancaster, UK
C. Antoine, CEA-IRFU, Gif-sur-Yvette, France L. Vega Cid, A. Sublet, G. Vandoni,
P. Vidal Garcia, W. Venturini Delsolaro CERN, Geneva, Switzerland E. Chyhyrynets, C. Pira
INFN/LNL, Legnaro, Padova, Italy
O. Kugeler, D. Tikhonov, HZB, Berlin, Germany
S. Leith, A.O. Sezgin, M. Vogel, University Siegen, Siegen, Germany
A. Medvids, P. Onufrijevs, Riga Technical University, Riga, Latvia

Abstract

The production of superconducting coatings for radio frequency (RF) cavities has been developed over several decades. It is widely accepted that for any further improvement in cavity RF performance, innovation is needed and one may have to turn to other forms of Nb and other superconducting materials. The potential benefits of using materials other than Nb would be a higher T_c and a potentially higher critical field H_c. This could lead to potentially significant cryogenic cost reductions if the cavity operation temperature is 4.2 K or higher. We report on optimising deposition parameters and the effect of substrate treatment prior to deposition, on successful synthesis of Nb and A15 superconducting thin film. The materials characterization is determined using scanning electron microscopy SEM, energy dispersive spectroscopy EDS, glancing X-ray diffraction GXRD, atomic force microscopy AFM and Rutherford backscattering RBS. The DC superconducting properties have been tested using Vibrating Sample Magnetometer VSM and Magnetic Field Penetration MPF. This work involves a team of 8 research groups in 7 different countries and is part of the H2020 ARIES collaboration.

INTRODUCTION

Radio-frequency (RF) cavities are used to accelerate charged particles in particle accelerators which can be used for a wide range of applications in science, health, safety, industry, etc. RF cavities made of superconducting materials, such as niobium, are currently the preferred solution. Niobium has the highest critical temperature (T_c = 9.25 K) and the highest superheating magnetic field H_{sh} of all the pure metals, also, it can easily be formed into the required cavity shape. The RF performance of bulk Nb cavities has continuously improved over the years, it is now approaching the optimal performance achievable ($H_{sh} \sim 210$ mT) [1-4]. However, they are quite expensive and operate at the theoretical performance limits of the material at temperatures below 2 K. Although further improvement has been achieved with nitrogen surface doping [2–4], long term solutions for SRF surface efficiency enhancement need yet to be pursued.

Thin films are the most economical way to modify surface properties to achieve enhanced performance, whether it is via single or multilayer configuration. The ultimate performance and efficient implementation of the thin film coatings depends on deposition parameters, deposition process and, most importantly, the substrate surface that is going to be deposited.

There are several physical properties that can affect the film's superconducting performance such as surface roughness, microstructure in terms of grain size and boundary, localise defects, residual stress and interfacial voids. It is a non-trivial process to separate and control the individual contributions from each of these factors. In order to achieve optimal performance in SRF cavities, it is necessary to understand the relationship of different deposition parameters on the formation of these factors and, consequently, on the superconducting properties of thin films.

In general, and particularly SRF thin film synthesis, other factor which has strong effects on the optimum superconducting performance is substrate material, substrate surface morphology as well as surface chemistry [5]. Lattice parameters a_0 were measured for films deposited onto the native oxide of copper and oxide free copper, producing similar a_0 of 3.3240 and 3.3184 Å respectively [5]. Niobium films grown on the oxidised copper substrate form grains which measure approximately 100 nm across, whereas grainsize is the order of microns on the oxide free substrate, resulting in larger RRR [6, 7].

Hence, for SRF thin film, surface preparation which includes surface treatment (to change the properties of surface in a desirable way) as well as cleaning (reduction of surface contamination to an acceptable level) is a major step. Surface preparation is an essential prerequisite for thin film synthesis. Rough or chemically impure surfaces adversely affect the nature of the thin film. A substrate that is flat, has sufficient grain size, and is chemically pure is the ideal starting point for thin film deposition.

As part of Horizon 2020 Integrated Activity ARIES program, we studied the effect of different substrate prepara-

* Work supported provided by European Union's ARIES collaboration H2020 Research and Innovation Programme under Grant Agreement no. 730871.
† reza.valizadeh@stf.ac.uk

ISBN: 978-3-95450-233-2 ISSN: 2673-5504 doi:10.18429/JACoW-SRF2021-FROFDV06

tion that are routinely practiced in the SRF cavity production, on the superconducting performance of PVD synthesised superconducting thin film of Nb as well high Tc superconducting material such as Nb_3Sn.

EXPERIMENTAL

OFHC copper sample were treated at CERN with chemical polishing (also known as SUBU5) solution and at INFN with SUBU5 solution, electro-polishing (EP), SUBU+EP, and tumbling [8]. The surface roughness after each procedure is tabulated in Table 1.

Table 1: Surface Roughness of Different Treatment of OFHC Copper for 1 mm Scan Length

Polishing treatment	Ra
Initial surface	127 ± 26 nm
SUBU5	48 ± 7 nm
EP	225 ± 80 nm
EP+SUBU5	115 ± 80 nm
Tumbling	48 ± 13 nm

The surface roughness was evaluated with Veeco Dektat 8 profilometer. EP treated substrate did not show any pitting or scratch marks on the surface. In contras tin both SUBU and EP+SUBU moderate amount of pitting was observed. Samples treated with tumbling procedure, the surface showed the roughness comparable to EP but there was considerable amount of scratches and inclusion of polishing media.

Nb thin film were deposited at three different centres (STFC, University of Siegen and INFN) [8,9], using DC magnetron and slightly different deposition parameters as shown in Table 2.

Table 2: Nb Thin Film Deposition Parameters

Parameter	STFC	Siegen	INFN
Deposit. temp. (➡C)	650	350	650
Target power (W)	400	400	400
Discharge gas	Kr	Ar	Ar
Op Pressure (mbar)	**1.5x10^{-3}**	**1.5x10^{-2}**	**5x10^{-3}**
Sub rotation	yes	no	no
Dep Time (min)	480	20	20
Dep rate (nm/min)	20	150	150

In all cases the target material was Nb target with *RRR* = 300. Although it was intended to keep all the parameters the same, however due to each facility capability the are some important differences in deposition parameters from one centre to another such as deposition temperature, pressure and rates that can have significant influence on mobility of adatoms which can promote a higher degree of growth zone in the structural zone model (SZM).

The synthesis of A15 superconducting thin film, Nb_3Sn, is performed using an alloy target with the 25 at% of Sn. The deposition power is chosen experimentally so the sublimation of Sn from target during deposition was at minimum taking into account the cooling water flow, temperature and deposition temperature. The deposition power 200 W in DC mode found to satisfy the condition.

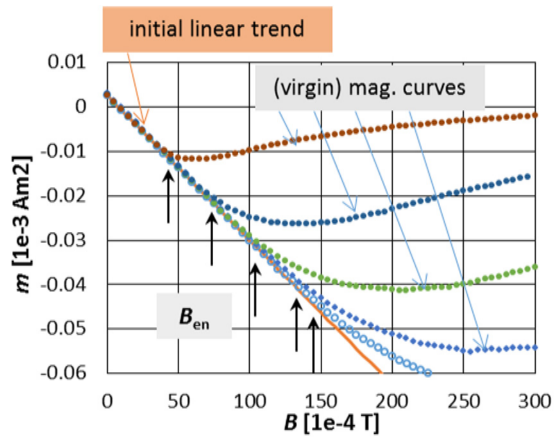

Figure 1: Illustration of determination of the characteristic field B_{en} from the virgin magnetization curves.

The magnetization measurements, the component of the magnetic moment (m) of the sample parallel to the external applied magnetic field B was measured, using Vibrating Sample Magnetometer (VSM) option of the commercial PPMS system from Quantum Design Inc. The magnetic moment m was measured in dependence on monotonically increasing (or decreasing) applied filed B, recording the so-called magnetization curves $m(B)$. The magnetization curves were measured on samples cooled down below T_c in zero applied magnetic field (zero-field-cooled conditions, ZFC). The external magnetic field was applied perpendicular to the flat face of the samples. The main characteristic determined from the magnetization curves is the so-called first flux entry field B_{en}. It is the applied field at which the magnetic flux starts entering the sample's volume.

It was detected as the field at which the virgin magnetization curve starts to deviate from the linear dependence that the virgin curve follows in the initial part starting from the zero applied field, as schematically illustrated in Fig. 1. The field B_{en} was determined employing 2% relative difference criterion, i.e. as the applied field at which the relative difference between the virgin magnetization curve and the initial linear trend reaches 2%. B_{en} is proportional to the first (lower) critical field B_{c1} through a geometrical constant that depends on the dimensions of the sample.

RESULTS

Nb Deposition in Single Layer

The SEM images of Nb deposited with parameters shown in table 2 for STFC conditions are depicted in Fig. 2. It displays the crystal grains size with well define boundaries of the copper substrate. Due to the high temperature

ISBN: 978-3-95450-233-2 ISSN: 2673-5504 doi:10.18429/JACoW-SRF2021-FROFDV06

deposition of 650 °C, the copper substrate has been annealed and large crystals of tens of microns developed. At this temperature the oxide layer is completely dissolved in the copper, and the Nb grains are influenced by the crystal orientation of the underlying copper. The surface consists of areas with different surface features characteristic of various grain orientations. The final crystal morphology seems to be independent of the type of substrate preparation.

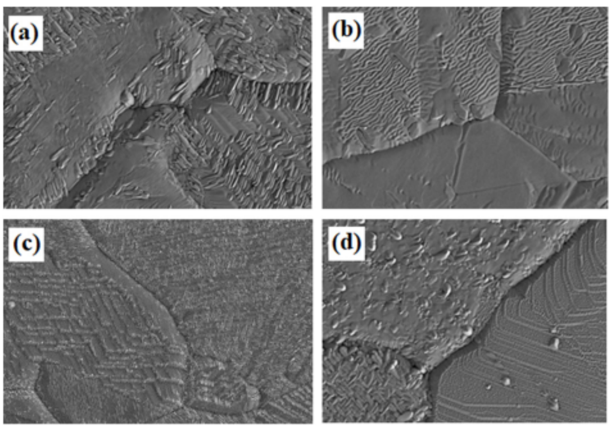

Figure 2: SEM images of Nb deposited with STFC deposition parameters (a) SUBU CERN, (b) EP + SUBU, (c) SUBU INFN and (d) EP.

The SEM images of films deposited at University of Siegen are depicted in Fig. 3. The film were grown with DC magnetron sputtering at temperature 350 °C which is 0.15 of niobium melting temperature. At 350 °C there is every chance that the surface of copper would be in the oxide state. The damage caused by sample preparation is still present in the top surface of copper. The surface dominated by small size grain as compared to large grain which has gone through annealing cycle at 650 °C. Figure 2 depicts growth consistent with Zone 1 of SZM growth model where film are grown in not a full density structure with some degree of longitudinal porosity. Although it is not at all obvious from SEM planar view but the film can contain a high level of dislocation density, hence a high level of residual stress also is expected.

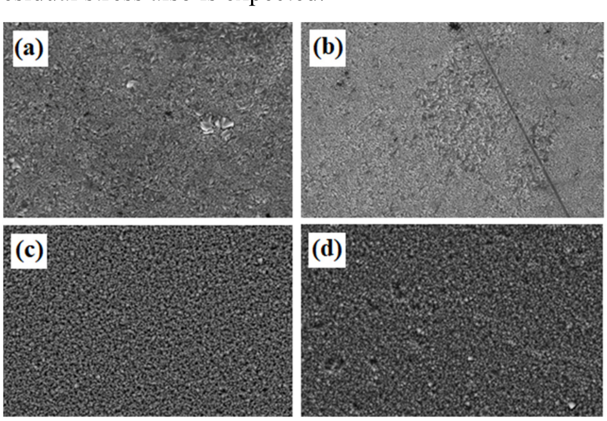

Figure 3: SEM images of Nb deposited with University of Siegen deposition parameters (a) SUBU CERN, (b) SUBU INFN, (c) EP and (d) EP + SUBU.

Figure 4 depicts the grazing incident X-ray diffraction of a Nb film deposited with the STFC deposition parameters on SUBU CERN prepared copper substrate. The analysis was done under conditions such that the substrate signal should have been totally suppressed. However, because of the small size of the analysed test piece which was used for squid magnetometer (2 x 2 mm^2) the edges of the sample were clipped by the x-rays resulting in the two major copper peak also being present. The results for Nb peaks correlate well with high purity Nb data and the film is grown in randomly oriented structure with slightly textured in (110) orientation. The lattice parameter was calculated to be 3.295 Å which is very close to bulk Nb. The grain size was determined to be around 51 nm.

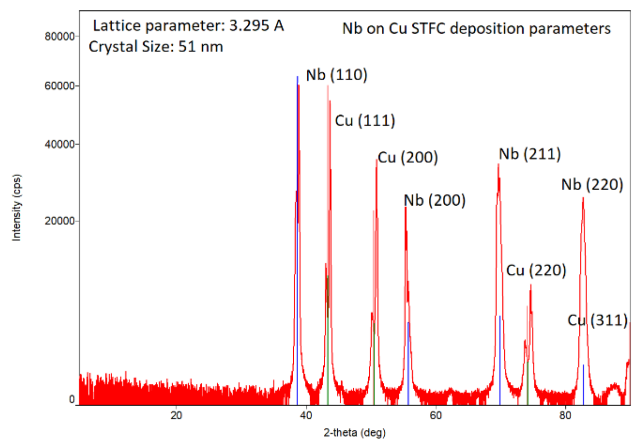

Figure 4: GXRD of Nb film deposited with the STFC deposition parameters on SUBU CERN prepared copper substrate.

The GXRD analysis of all the films grown on different prepared copper substrate were almost identical. This correlates very well with results of SEM observation that the growth of Nb film under the same condition is independent of the various substrate preparation.

Figure 5 displays the overview of firs flux entry B_{en} for all the samples in the series. It depicts that the correlation between the highest Ben and surface preparation method is inconclusive. The highest value of Ben measured were in the series that were from the STFC batch (C7, L13, L18 and L19) of deposition for both parallel and perpendicular field, where the deposition was done at 650 ➡C with the lowest deposition rate 20 nm/min. The highest registered Ben in the STFC batch was the sample which was prepared by SUBU at CERN. The sample batch deposited at the University of Siegen where the deposition temperature was the lowest in these set of sample at 350 ➡C, registered the lowest values of B_{en} ranging from 250 to 500 Oe. However, the highest value was for a sample prepared by SUBU at CERN. The batch of samples deposited at INFN which were deposited at 650 ➡C and the highest deposition rate of 150 nm/min, showed no dependence on the preparation method and averaged out around 400 Oe. The lowest measured B_{en} was found to be for samples deposited on substrates prepared by EP followed by SUBU (L16, L18, L19).

ISBN: 978-3-95450-233-2 ISSN: 2673-5504 doi:10.18429/JACoW-SRF2021-FROFDV06

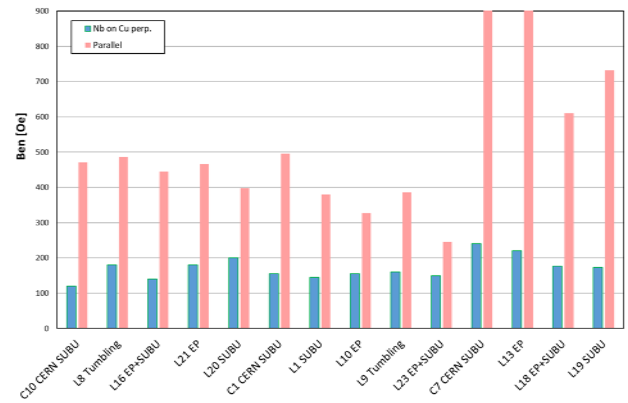

Figure 5: Overview of the first flux entry fields of B_{en} for the non-Nb films on Cu substrates measured on VSM.

The superconducting performance was also evaluated with filed penetration facility which was designed and built at STFC [10]. The results of sample evaluations with a full flux penetration field (B_{fp}) are shown in Fig. 6.

It was observed that both SUBU and EP had a larger B_{fp} individually that both treatments together. In addition, it can be seen that the reduction due to the EP + SUBU is more pronounced in the samples from INFN and the University of Siegen. It also confirms that SUBU method produced the highest B_{fp}. A comparison of these full field penetration with the results from VSM analysis showed some correlation with STFC deposition where the film was grown at high temperature and larger thickness (10 ↘m).

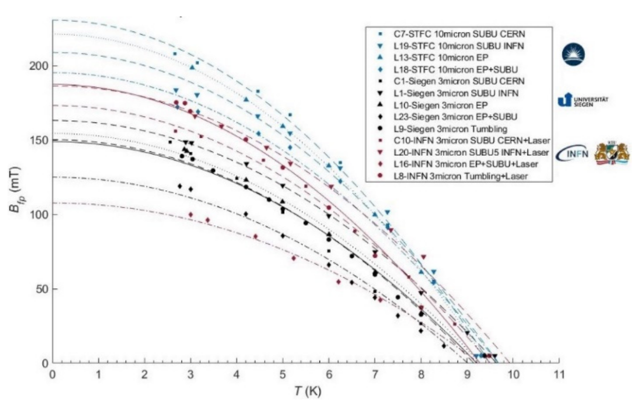

Figure 6: Overview of the field of full magnetic flux penetration (B_{fp}) for the Nb films on Cu.

Nb_3Sn Deposition in Single Layer

The Nb_3Sn is an intermetallic compounds and is extremely brittle in the solid bulk form. In order to produce an RF cavity using such a material it is possible only by depositing a thin layer on the inner surface of an already formed cavity. The superconducting parameters, such as T_c, Δ, H_{c2} depends strongly on the Sn content [11] and as a results in perfect ordering in the stoichiometry phase, ρ_n drops below 20 μΩcm. Therefore R_{BCS} for Nb_3Sn has the potential to be either much lower or much higher than for Nb. Optimising the deposition parameters such as deposition power, substrate temperature and deposition rate it is possible to synthesis stoichiometry A15 phase with relative ease.

Nb_3Sn films were deposited on an oxygen-free, high-conductivity (OFHC) copper substrate without any surface chemical polishing preparation. The deposition was carried out at 500, 450 °C and at room temperature. For the latter, the substrate was heated to 550 °C for 20 hours and then cooled to room temperature prior the deposition and then annealed at 550 °C post deposition for 20 hours. The film composition was found to be independent of the deposition temperature and corresponding to a superconducting phase Nb_3Sn composition. The film deposited at room temperature showed no sign of superconductivity until it was annealed to 550 °C and had a value for B_{en} ⬆ 100 Oe.

After annealing the surface was covered with a deep network of cracks, shown in Fig. 7a, which is not at all suitable for SRF application. The film deposited at 450°C was found to be superconducting with a Tc of 14.6 K and B_{en} of 250 Oe. The T_c was improved and increased to 15.7 K when the deposition was carried out at 550 °C. To achieve the near to theoretical value of 18 K all other samples were deposited at 650 °C whilst insuring that the extra added temperature to the system is well within the acceptable condition where the composition of alloy Nb_3Sn target stays unchanged. Of all samples grown at 650 °C, the T_c was measured to be 17.5 K on copper and slightly higher at 17.75 K on sapphire. As shown in Fig. 7b.

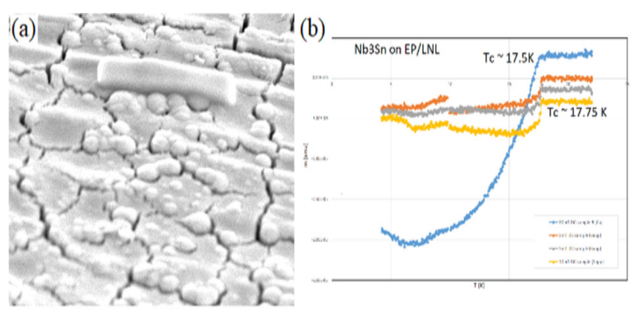

Figure 7: SEM plan view of Nb_3Sn film (a) deposited at room temperature and annealed to 550 °C, (b) Critical transition temperature for film deposited at 650 °C.

A series of Nb_3Sn thin film were directly deposited on various copper sample treated with EP and SUBU which were prepared at STFC and INFN. All the films were deposited at 650 °C, The results of the first flux entry in B_{en} are displayed in Fig. 8.

All the films grown in this series had the same superconducting phase with a +/–2% composition as determined both by energy dispersive spectroscopy EDS and Rutherford back scattering RBS. The resulting first flux entry varied from 400 to 1000 Oe with no correlation with sample preparation condition. The observed M-H plot at 4.4 K display very hysteretic nature with no flux Jump behaviour as shown in Fig. 12a. Nevertheless the hysteresis in the M-H curve indicates the existence of strong pinning centres for the flux-lines inside the bulk. The higher critical magnetic field H_{c2} was never reached due to the maximum field of the VSM which was 16 T.

ISBN: 978-3-95450-233-2 ISSN: 2673-5504 doi:10.18429/JACoW-SRF2021-FROFDV06

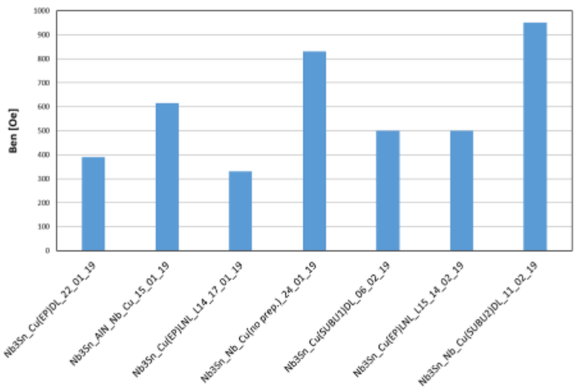

Figure 8: Overview of the first flux entry fields of Ben for the non-Nb films on Cu substrates measured on VSM.

X-section and plan view SEM depicted that the transition at the interface is very smooth and film is grown in a very dense structure as can be seen in Fig. 9a and b. The EDS mapping of the X-section is shown in Fig. 9c, no inter-diffusion of substrate and film material is noticeable. However across the thickness of the film broken dark lines and light area are extended from the surface to the interface which can be interpreted as an area of Sn deficiency or region of excess Sn respectively. These area may be normal conducting or superconducting with lower performance, their influence on the total behaviour of the superconducting film in a RF field is not yet determined and needs to be studied further by either directly deposited in a cavity or the use of quadrupole resonator.

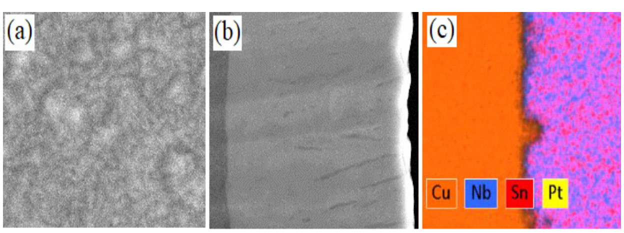

Figure 9: SEM and EDS analysis of Nb3Sn deposited at 650°C on SUBU processed copper sample at STFC (a) plan view SEM, (b) X-section view and (c) EDS mapping of the SEM X-section.

The crystal structure of the film was examined with GXRD. The result is shown in Fig. 10. As well as the major peaks of Nb3Sn there are two copper peaks corresponding to (111) and (200) orientation which is due to small size of the analysed sample where the edge of the sample was clipped. The analysis of the peaks determined that the film crystal structure is of the superconducting phase with lattice parameter a0 = 5.315 Å which is slightly higher than the theoretical value of 5.295 Å reported in literature. The grain size is estimated to be 17 nm and crystallinity of 85%.

To assess the likely performance of Nb_3Sn deposited on a Nb cavity as an enhancement to a pure Nb cavity, a bilayer of Nb/Nb_3Sn was made. A sample was synthesised by depositing Nb_3Sn of top of 2.6 µm of Nb on SUBU prepared copper substrate at 650 °C. Figure 11 shows the X-section SEM and its corresponding EDS elemental mapping of the bilayer deposition resulted in two different.

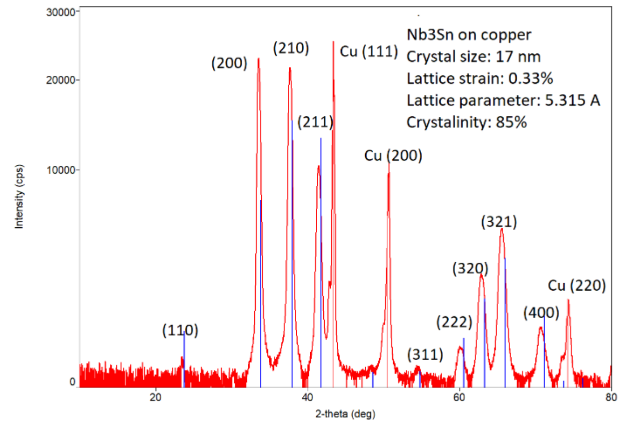

Figure 10: GXRD spectrum of Nb_3Sn film deposited at 650 ➡C on a SUBU prepared copper sample.

To assess the likely performance of Nb_3Sn deposited on a Nb cavity as an enhancement to a pure Nb cavity, a bilayer of Nb/Nb_3Sn was made. A sample was synthesised by depositing Nb_3Sn of top of 2.6 µm of Nb on SUBU prepared copper substrate at 650 °C. Figure 11 shows the X-section SEM and its corresponding EDS elemental mapping of the bilayer deposition resulted in two different.

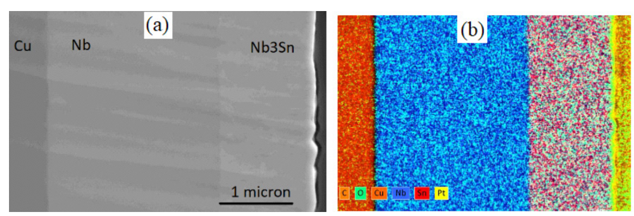

Figure 11: (a) X-section image of the Nb_3Sn deposited with a Nb by-layer on SUBU prepared copper sample, (b) corresponding EDS elemental mapping of the layers.

It depicts a sharp interface between the substrate copper and the Nb by-layer and also between Nb and the top Nb_3Sn layer. The EDS mapping shows a homogenous composition through each corresponding layer with no interdiffusion of elements and the Nb_3Sn has the A15 composition of 24.5 %.

Figure 12 b present isothermal magnetisation (m) versus magnetic field (H) plots for the by-layer.

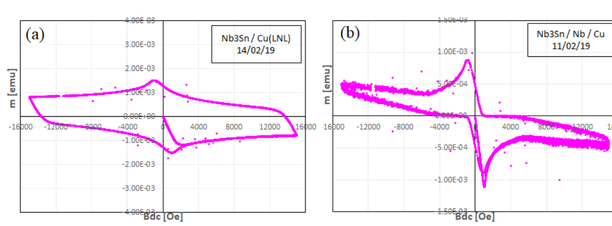

Figure 12: Isothermal magnetisation (m) versus field (H) plots for (a) single layer Nb_3Sn deposited on copper and (b) by-layer of Nb/Nb_3Sn deposited on copper.

A comparison of between the single layer and the by-layer demonstrate a significant improvement in the magnetisation respond. In the hysteretic nature has been reduced considerably. In the high filed region of the M-H plot, in the return field path, M remains invariant to H

ISBN: 978-3-95450-233-2 ISSN: 2673-5504 doi:10.18429/JACoW-SRF2021-FROFDV06

which demonstrate a Bean-Livingston surface barrier [12] for the flux line inside the layer. Consequently a higher first flux B_{en} = 98 mT is calculated as it is displayed in Fig. 7.

CONCLUSION

To optimise the superconducting performance of Nb and A15 superconducting thin film, we investigated the effect of different substrate preparation commonly in practice for cavity production such as EP, SUBU and tumbling combined with different deposition parameters on the superconducting properties of the synthesised thin film.

Although not conclusively it was found SUBU and EP are the best method or preparing the copper substrate. EP plus SUBU was found to reduce the superconducting properties of the deposited film considerably irrespective of film deposition parameters employed in this investigation. The best result for Nb thin film on copper was produced when the film was deposited at highest 650 °C and deposition rate of 20 nm/min. These were the highest temperature and the lowest deposition rate employed in this investigation.

Nb_3Sn can be successfully deposited from an alloy target and demonstrate good SC properties when it is deposited at high temperature (around 650 °C). The T_c was strongly dependent on the temperature of deposition temperature and the optimum temperature was found to be 650 °C where a T_c = 17.75 and 17.5 K was achieved on sapphire and copper.

The superconducting properties of Nb_3Sn film considerably improves with a Nb buffer layer between the copper and the A15 superconductor.

REFERENCES

[1] A. Gurevich, “Enhancement of RF breakdown field of superconductors by multilayer coating,” *Appl. Phys. Lett.,* vol. 88, p. 012511, 2006. doi:10.1063/1.2162264

[2] P. Dhakal *et al.*, “Effect of high temperature heat treatments on the quality factor of a large-grain superconducting radio-frequency niobium cavity,” *Phys. Rev. Spec. Topics Accel. Beams,* vol. 16, p. 042001, 2013. doi:10.1103/PhysRevSTAB.16.042001

[3] A. Grassellino *et al.*, “Nitrogen and argon doping of niobium for superconducting radio frequency cavities: a pathway to highly efficient accelerating structures,” *Supercond. Sci. Technol.,* vol. 26, p. 102001, 2013. doi:10.1088/0953-2048/26/10/102001

[4] G. Ciovati, P. Dakhal and A. Gurevich, “Decrease of the surface resistance in superconducting niobium resonator cavities by the microwave field,” *Appl. Phys. Lett.,* vol. 104, p. 092601, 2014. doi:10.1063/1.4867339

[5] C. Benvenuti, S. Calatroni, P. Durriulat, M. A. Peck and A. M. Valente, “Fluxon pinning in niobium films,” *Physica C,* vol. 351, p. 429, 2001. doi:10.1016/S0921-4534(00)01646-4

[6] C. Benvenuti, S. Calatroni, P. Darriulat, M. A. Peck, A.-M. Valente, and C.A.Van’t Hof, “Study of the residual surface resistance of niobium films at 1.5 GHz,” *Physica C: Superconductivity,* vol. 351, p. 421, 2001. doi:10.1016/S0921-4534(00)01645-2

[7] C. Benvenuti, S. Calatroni, M. Hakovirta, H. Neupert, M. Prada, and A. M. Valente, “CERN studies on niobium-coated 1.5 GHz copper cavities,” *The 10th Workshop on RF Superconductivity*, Tsukuba, Japan 2001.

[8] C. Pira *et al.*, “ARIES Deliverable Report 15.1”, 2018.

[9] C. Pira *et al.*, “Impact of the Cu substrate surface preparation on the morphological, superconductive and RF properties of the Nb superconductive coatings”, *in Proc. SRF 2019, Dresden, Germany*, p. 935-940, 2019. doi:10.18429/JACoW-SRF2010-THP041

[10] D. Turner *et al.*, “A Facility for the Magnetic Characterisation of Planar Thin Film Structures”, *in Proc. SRF 2021*, virtual conference, 2021, SUPFDV007.

[11] M. Mentink *et al.*, “Superconductivity in Nb-Sn thin film of stoichiometric and off-stoichiometric composition,” *IEEE Transactions on Applied Superconductivity,* vol. 23, p. 7100505, 2013. doi:10.1109/TASC.2012.2235513

[12] C.P. Bean and J.D. Livingston, “Surface Barrier in Type-II Superconductors,” *Phys. Rev. Lett.,* vol. 12, p. 14, 1964. doi:10.1103/PhysRevLett.12.14