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ELECTROCHEMICAL DEPOSITION OF Nb_3Sn ON THE SURFACE OF COPPER SUBSTRATES

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Abstract

Coating superconducting Nb_3Sn thin film on the inner surface of a superconducting RF cavity is one of the most promising approaches to improve the performance of the accelerating cavity. In addition, depositing Nb_3Sn on Cu cavities can further benefit from copper cavities' high thermal conductivity and mechanical stability. Compared with traditional sputtering processes, electrochemical coating has the advantages on process simplicity, low cost and mass production. However, the conventional electroplating, because of its low growth temperature and aqueous reaction environment, tends to produce porous, loosely bonded, and often contaminated film. All these properties result in excessive pinning center and deteriorate the superconducting radio frequency cavities' performance. In this paper, a new method including multi-layer electroplating and heat treatment is used to deposit Nb_3Sn thin film on top of copper substrates. Important growth parameters, e.g. electrical current density, layer thickness ratio, and annealing temperature are studied. The morphology of the film surfaces was observed by scanning electron microscope (SEM) and the structure of the film was analyzed by X-ray diffraction (XRD). The results showed that a flat and uniform Nb_3Sn layer on copper can be obtained, and the thickness is about 7 μm.

INTRODUCTION

In order to realize high quality Nb_3Sn coating on copper, different methods have been developed by the thin film SRF community worldwide. So far, most researchers rely on preparing niobium-tin mixed precursor, either by sputtering from a stoichiometric Nb/Sn powder pressing target [1], or by alternatively sputtered Nb/Sn multilayer structure [2, 3], or by Nb/Sn double target co-sputtering [4], and then followed by low temperature an-nealing, either *in-situ* or *ex-situ*, to prepare Nb_3Sn coat-ing on copper. Some other endeavors have been made through CVD [5] and MOCVD [6] methods. Using Nb/Sn halides or organic Nb/Sn compounds, Nb-Sn mixture thin films can be successfully deposited on copper.

However, all films generated from the above methods end up in non-stoichiometric state and contain lots of non-Nb_3Sn phases. The low annealing temperature lim-ited by copper's melting point was the biggest obstacle for the synthesis of good-quality Nb_3Sn film. Because of the stoichiometry is off, the of those films featured low T_c below 17 K, high RF loss, and inferior RF per-formance which cannot meet the demand of supercon-ducting RF applications. It is very difficult to obtain Nb_3Sn thin films on copper by direct niobium-tin reac-tion at present stage.

Recently, thin film RF superconducting researchers have been inspired by the preparation process of Nb_3Sn cable. Copper was introduced into niobium-tin reaction system [7], and niobium-tin binary reaction was trans-formed into copper-niobium-tin ternary reaction. Cop-per-tin-copper multilayered structure deposited on nio-bium substrate by Fermi laboratory was successfully converted to bronze / Nb_3Sn / unreacted niobium struc-ture after low temperature heat treatment [8, 9]. At 700℃ for 100 hours, a Nb_3Sn layer with a thickness of 1~4 μm and a high T_c of 17.6 K could be obtained. The bronze formed by the reaction covered the surface of the sample during the heat treatment process, which reduced the chance for tin to escape from the reaction system and facilitated the formation of Nb_3Sn.

In this paper, a method of plating Nb_3Sn on copper substrate is proposed. First, a thick niobium layer is de-posited on copper substrate by magnetron sputtering, and then Nb_3Sn coating is obtained by combining elec-troplating and heat treatment. The electroplating is car-ried out at ambient temperature and pressure, and the heat treatment is carried out in quartz tube annealing fur-nace. A few Nb_3Sn film on copper samples has been pro-duced according to the recipe above. The characteriza-tion of these samples, including SEM and XRD, is in-cluded in this paper. The results are encouraging and showed that there were Nb_3Sn phase with thickness up to 7 μm formed after the annealing.

THIN FILM COATING SETUP

The dimensions of copper substrates were 10 x 10 x 1 mm. All substrates were cut from one OFHC copper sheet. After receiving from the machineshop, the copper substrates were electro-polished with n-butnol and sul-phuric acid mixture. The average roughness was below 200 nm. Before each run of the experiments, substrates were first rinsed with diluted hydrogen chloride acid to remove oxide layers on the surface, then they were washed with deionized water and preserved in anhy-drous ethanol. As the initial coating step, a layer of 3 μm thick niobium was

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deposited on copper by ~ 3 hours magnetron sputtering. Then, a thin copper / tin / thick copper multi-layer structure was deposited on top of the Nb film via electrochemical plating. During the plating, electrochemical analysis was carried out by *Constant Current V-T curve*. The morphology of the film (as-deposited and annealed) was observed by SEM. The film composition was investigated by Energy Dispersive X-Ray Spectroscopy (EDX) analysis. The structure of the film was analysed by XRD using a Rigaku D/max-2400 instrument. XRD was performed in the 2θ angular range of 10–90°.

Electro-deposition of Cu and Sn Layers on Cu/Nb Substrates

An aqueous solution of pyrophosphate-based electrolyte was employed for both the thin copper (diffusion) layer and thick copper (barrier) layer whose composition is reported in Table 1. The temperature for depositing both copper layers was room temperature (about 24 ℃), the current density was 40 mA/cm^2, and the plating time was 0.5 minutes and 3 minutes, respectively. The PH value was controlled between 8.0 and 8.8. The electrodeposition of tin was performed using a sulphate-based electrolyte whose composition is reported in Table 2 at a current density of 40 mA/cm^2 and room temperature. Chemical reagents used in the electrolytes were all analytical grade. The magnetic stirring rate during the reaction was 200 r/min.

Table 1: Composition of Electrolyte used for the Deposition of the Copper Layer

Chemicals	Concentration (g/l)
$Cu_2P_2O_7$	20
$NaNO_3$	5
$Na_4P_2O_7$	175
$C_6H_{17}N_3O_7$	15

Table 2: Composition of Electrolyte used for the Deposition of the Tin Layer.

Chemicals	Concentration(g/l)
$SnSO_4$	25
H_2SO_4	50ml/l
$C_4H_6O_6$	12
$C_4H_8O_6$	1.5

Heat Treatment of Cu/Nb/Cu/Sn/Cu Samples

The heat treatment was carried out in a small tube furnace. Fig. 1 shows the temperature control curve of heat treatment. First, the temperature was raised to 214 ℃, slightly below the melting point of tin, and then kept for 50 hours to let the diffusion occur between the copper and tin and form bronze. Then, the sample was heated up to 458 ℃ for 10 hours, during which the liquid tin phase was formed, and the tin diffused into niobium through bronze-niobium interface. Finally, the temperature rise to 700 ℃ for 24 hours to let Nb react with Sn and form Nb3Sn phase.

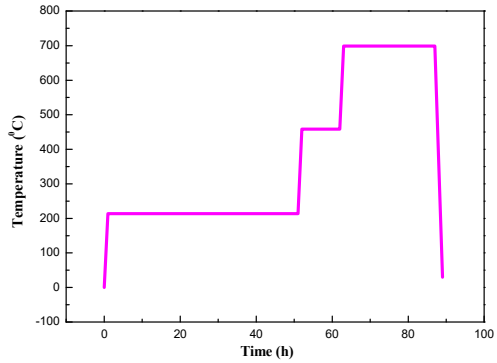

Figure 1: Temperature Control Curve of Heat Treatment.

Constant Current V-T Curve of Cu/Nb/Cu/Sn/Cu Samples

Fig. 2 shows the constant current V-T curve of niobium electrode in pyrophosphate copper plating solution. In the figure, the constant current corresponding to curve a, b, c, d is 20, 30, 40, and 50 mA/cm^2, respectively. How-ever, the precipitation potential of copper is -1.6V, -2.0 V, -2.3 V, -3.0V. When the current is 40 mA/cm^2, the activation degree of the substrate is high and the plating uniformity is fast. Fig. 3 shows the constant current V-T curve of copper electrode in sulphate-based tin plating solution. In the figure, the constant current correspond-ing to curve e, f, g, h is 20, 30, 40, and 50 mA/cm^2, re-spectively. However, the precipitation potential of tin is -0.51V, -0.53V, -0.61V, -0.53V. When the current is 40 mA/cm^2, the activation degree of the substrate is high and electroplating uniformity is the best.

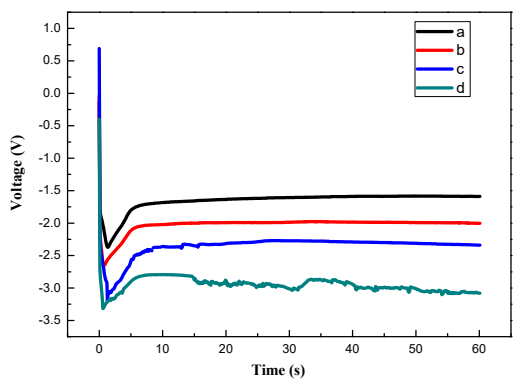

Figure 2: The Constant Current V-T Curve of Niobium Electrode.

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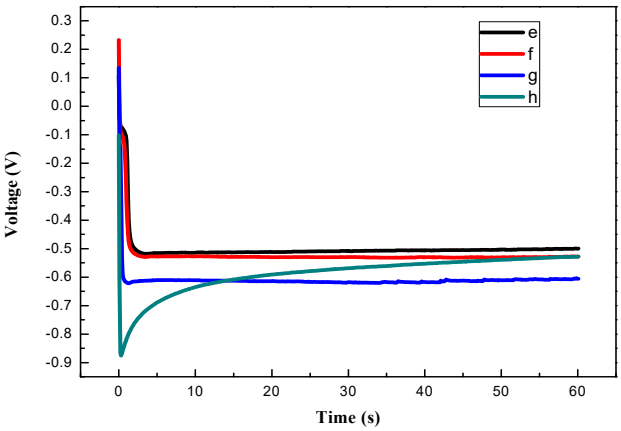

Figure 3: The Constant Current V-T Curve of Copper Electrode.

Characterization of Cu/Nb/Cu/Sn/Cu Samples

Cu/Nb/Cu/Sn/Cu samples after thermal treatment were characterized by means of SEM, XRD and electrical tests. The surface morphology and cross-section of the film layer are tested by SEM. It can be seen from the Fig. 4 that the grain distribution of the surface deposits is generally uniform, but there are convex and concave areas in the individual areas, resulting in low surface smoothness. It must be noted that the cross section sample was ground with 1-2 microns grinder to expose the longitudinal cross sections for film thickness measure-ment. The thickness of the Nb_3Sn alloy was about 7.0 μm.

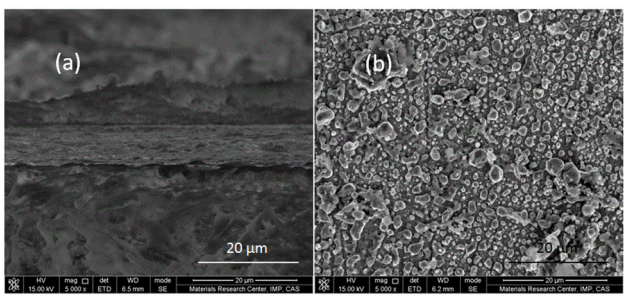

Figure 4: (a) SEM image of the cross section view. (b) SEM image of the surface.

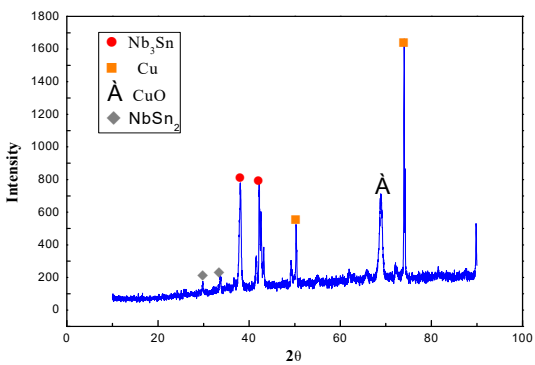

Figure 5: XRD characteristic Curve of thin film.

XRD measurement was performed with a Rigaku D/max-2400 at 2θ angular range from 10 to 90°. The XRD pattern in Fig. 5 shows the reflection of a crystalline cubic Nb_3Sn phase (A15 structure). Other reflections can be attributed to $NbSn_2$, and CuO. In particular, cubic Nb_3Sn having strong (211) preferred orientation (P.O.), disordered orthorhombic $NbSn_2$ phases were observed.

SAMPLES RESULTS

The results of the synthesis of Nb_3Sn thin films onto Cu substrates were presented herein. Superconductive coatings were obtained by combining thermal treatments and the electrochemical technique for thin film deposition. And vertical tests of the cavity showed that a flat and uniform Nb_3Sn layer on copper can be obtained, and the thickness is about 7 μm. The next step of this research, including the superconductivity and RF performance will be tested and the potential of RF superconducting cavity will be analyzed. The primitive model for Cu-Nb-Sn ternary reaction is established, the growth parameters are controlled quantitatively, and the Nb_3Sn coating samples with quality up to standard are completed. Effective control of coating parameters, guiding development of 1.3G copper cavity plating Nb_3Sn thin films.

CONCLUSION

The successful synthesis of Nb_3Sn thin films on copper substrates provides the possibility for the next step in RF superconducting cavity. However, there are still some key issues that need to be addressed. The main of which are mechanical and/or chemical polishing tech-niques will have to be used to remove the superficial bronze layer about 10 μm thick, and expose the super-conducting Nb_3Sn film as RF working surface. The rel-atively large thickness of the Nb_3Sn layer produced will offer sufficient margin for the use of electropolishing, which can be controlled with 1 μm accuracy [9].

REFERENCES

[1] G. J. Rosaz, "A15 material development at CERN," presented at the 2nd SRF Thin Film Working Group Meeting, Geneva, Switzerland, 2016.

[2] M. N. Sayeed, "Nb_3Sn Multilayer Sequential Sputtering Update at Jefferson Lab," in TFSRF2018, Legnaro, Italy, 2018.

[3] J. Li, "Magnetron sputtering of Superconducting Multilayer Nb_3Sn Thin Film," Master, Surface Treatments for Industrial Applications, University of PADOVA, 2010.

[4] G. J. Rosaz, S. Aull, E. A. Ilyina, A. Sublet, and W. V. Delsolaro, "SRF Cavity Coatings: Review of Alternative Materials and Coating Techniques," in *Proc. SRF2017*, Lanzhou, China, 2017, p. WEXA04.

[5] R. E. Enstrom and J. R. Appert, "Preparation and high-field superconducting properties of vapor-deposited Nb_3Sn alloys," *J. Appl. Phys.*, vol. 45, pp. 421-428, 1974.

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[6] G. Carta, G. Rossetto, P. Zanella, L. Crociani, V. Palmieri, and F. Todescato, "Attempts to deposit Nb3Sn by MOCVD", 2006.

[7] S. Franz, E. Barzi, D. Turrioni, L. Glionna, and M. Bestetti, "Electrochemical synthesis of Nb_3Sn coatings on Cu substrates," *Materials Letters,* vol. 161, no. 1, pp. 613-615, 2015.

[8] Emanuela Barzi, "State-of-the-art Nb_3Sn Films by Electrochemical Deposition," in TFSRF2018, Legnaro, Italy, 2018.

[9] E. Barzi, M. Bestetti, F. Reginato, D. Turrioni, and S. Franz, "Synthesis of superconducting Nb_3Sn coatings on Nb substrates," *Superconductor Science & Technology,* vol. 29, no. 1, p. 015009, 2016.