Investigations Towards Ultra-Low Cost Nb_3Sn SRF Cavity Fabrication via Melt Casted Bronze Route Processing

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***Abstract*—A novel approach to fabricating Nb_3Sn SRF cavities and other RF components using an ultra-low-cost melt casting fabrication process has been investigated. This simple, low cost melt casting technique has the potential to be used to fabricate nearly any superconducting Nb_3Sn structure using either the Bronze Route (BR), Internal Tin (IT), External Tin (ET) processes as well as normal conducting pure copper (Cu) cavities.**

Most of the heat treated samples that were examined using SEM/EDX seemed to show a reasonable correlation of T_c onset and transition width (ΔT_c) of the ingots initial/starting Sn content to the desired stoichiometric Nb_3Sn phase, where the lower starting Sn content coupons resulted in lower T_c's with broader transition widths and the higher starting Sn coupons resulted in higher T_c's with narrower ΔT_c's. The best samples had T_c onsets ~17-18 K and ΔT_c's < 2 K. Two samples were further tested for RF surface resistance (R_s) and Quality Factor (Q) at JLAB. These RF measurements were performed at 7.4 GHz using a calorimetric technique and showed two transitions, one at ~ 8 K and another at ~ 14 K; values of R_s were at least two orders of magnitude higher than similar high quality Nb_3Sn films directly deposited substrates by JLAB and with another superconducting transition close to the superconducting transition temperature of niobium. Substantial improvements in the processing variables ranging from higher quality of the initial ingots with higher Sn content, to better electropolishing and reaction heat treatment regimens will be necessary to realize improved RF performance metrics.

Index Terms— Bronze Route, Nb_3Sn, SRF Cavity

I. Introduction

Energy to Power Solutions (e2P) in collaboration with the Thomas Jefferson National Accelerator Facility (JLAB), ExOne Corporation,[1] and the Hackett-Brass Foundry,[2] investigated a novel approach to Nb_3Sn SRF cavity fabrication using synergistic technologies consisting of high quality Nb thin films deposited using (JLAB's) Electron Cyclotron Resonance (ECR) RF sputtering on low cost bulk "melt-casted" bronze (Cu-Sn) substrates/coupons. The starting bronze substrates were obtained using a two-step fabrication process consisting of first 3D printing a "sand mold" and then subsequently melt casting the bronze substrate using the 3D printed sand mold. A single-step process involving direct metal 3D printing with subsequent molten "bronze infusion" although possible, was not selected due to its far higher cost and significantly longer fabrication time.

e2P's patent pending Nb_3Sn SRF cavity fabrication process (see US 62/087557 and 62/631,067) can be thought of as the "inverse" process of existing state-of-the-art technology[3] (i.e. Sn diffused into a bulk Nb cavity). In our modified Bronze Route (BR) process, the Sn content is provided by a near "infinite" reservoir from the underlying low cost (<$3/lb) bulk bronze (Cu-Sn) scaffold via high temperature reaction diffusion and the higher cost Nb is provided via (thin ~ 1μm) film ECR deposition. In this study, multiple samples from five starting Cu:Sn alloys (89%Cu:11%Sn, 87%Cu:13%Sn, 86%Cu:14%Sn, 85%Cu:15%Sn, and 81%Cu:19%Sn) were subjected to our modified BR Nb_3Sn fabrication process, which is summarized in section II-A. The technical feasibility of each step of our BR process was investigated on coupon sized samples. Thus far, the technical viability of the melt casting process appears to be encouraging and worthy of further study since our two-step melt casting technique can be similarly extended to pure Cu RF structures as well. If pure Cu cavities can be fabricated using our two-step process (i.e. 3D printed "sand" mold + Cu melt casting), this opens up the possibility of Nb_3Sn SRF cavity fabrication via the more complex Internal Tin (IT) and External Tin (ET) processes as well as normal conducting Cu cavities and other related RF components. The melt casting process itself is well understood and dates back millennia. If technical viability can be shown, this technique could be used to fabricate large, complex structures (e.g. 9-cell RF cavity), at very low costs; however significant technical challenges remain for RF applications.

II. Experimental

A. Processing Parameters

At a high level, the seven step process used to fabricate the samples/coupons in our investigation is summarized below.

Step 1: 3D Printing of Sand Molds for Bronze Substrates
Step 2: Melt Cast Bronze Substrates in Sand Molds
Step 3: Mechanical/Electro-Polishing Casted Substrates
Step 4: Deposit Nb Thin Films on Bronze Casted Substrates
Step 5: In Situ or Ex-Situ Post Reaction Heat Treatment
Step 6: Test & Evaluate

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Step 7: Repeat process for DC/RF materials optimization

Our novel Steps 1 and 2 were quite straight forward, and from start to finish these two steps took < 1 week to fabricate all samples used in the investigation, with the majority of the time lost in shipping the samples from one place to the next. Optimzing the multitude of parameters and processing variables involved in Steps 3, 4 and 5 to obatin the correct Nb_3Sn stoichiometric ratio with good DC/RF properties were the key technical challenges in our initial 6 month investigation and where future R&D efforts should concentrate. Unfortunately, although there is extensive information available in the technical literature for each of these three steps (e.g. electro-polishing, Nb film deposition, and heat treatment) direct application to our modified BR process for SRF applications was not straightforward. For example, in Step 3, the vast majority of the literature for electro-polishing on pure Cu substrates proved of limited value as the established procedures developed for pure Cu cavities were for the most part inadeqaute for the bronze substrates. Furthermore, the diffusion reaction heat treat regimens developed over decades[4] for BR wire processing[5],[6],[7],[8] were mostly geared towards small grains (hence high J_c) operating in the vortex state[9] and not the desired larger grains used in SRF applications.[10]

In summary, e2P processed twenty 10x10 mm square samples for T_c measurements and thirteen 2" round samples for RF measurements. All of the 10x10 mm square substrates (cut from the original 2" diameter samples) and four of the thirteen 2" round substrates had their Nb films deposited with ECR at JLAB using high bias voltages (i.e. incident ion energies) of -60 V and -120 V. The remaining nine 2" diameter round samples had their Nb films~ (~1μm) deposited with the more common low ion energy (< 10 eV) RF sputtering. In this paper, we only report measurement data and analysis on the bronze substrates with Nb films deposited with ECR at JLAB. The remaining nine samples with low ion incident energy RF sputtering were not heat treated due to time and fiscal limitations.

Processing variables investigated included: a) bronze type (Cu:Sn ratio), b) heat treatment temperature (700-800°C),[11] c) heat treament environment vacuum vs. inert Argon, and d) Nb film deposition bias voltage (i.e. ECR ion incident energy). To avoid any ambiguity, a pure Nb film was deposited on each bronze substrate via the high ion energy ECR process, and not a Nb_3Sn film. The Nb coated bronze substrates were then heat treated/reacted in a separate reaction furnace (i.e. "Ex-Situ") to allow the Sn from the bronze to diffuse into the Nb via the BR solid state reaction process. Unfortunately, "In-Situ" BR processing with elevated bronze substrate temperatures (i.e. 100°C →900°C) was not possible during this initial investigation for a variety of reasons including the concern over possible contamination of JLAB's ECR chamber. Subsequent R&D investigations should definitely explore this processing variable to determine its potential impact on Nb_3Sn stoichiometry, grain structure, and ultimately DC/RF properties.

B. Sample Preparation

To better understand our Nb_3Sn BR fabrication approach, a typical sample preparation process is described. In the first step of the process, a 3D CAD drawing of the desired object is made. Once converted to the appropriate file type, the CAD drawing is sent to the 3D printer which then prints a "sand mold" for the object. In our investigation, two types of sand molds were fabricated: a) 2" diameter round substrates/coupons and b) dog-bone shaped samples for ASTM E8 tensile testing (see Fig. 1).

Fig 1: Bottom half of 3D printed sand molds

The sand molds were then used to melt cast the bronze coupons and subsequently discarded after one use. Of the five starting bronze ingots, only the 89/11 was commercially available. The remaining four bronze ingots with the higher starting Sn content had to be specially fabricated for this study. This turned out to be a serious detriment, since the quality of these R&D grade samples was quite poor possessing numerous pores, pits, and unevenly mixed Sn throughout its entire cross section (see Fig. 2).

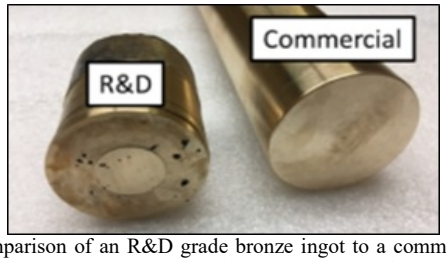

Fig. 2: Comparison of an R&D grade bronze ingot to a commercial grade ingot. Note, the numerous pits and inadequate mixing of the starting Sn.

After the coupons had been melt casted into the 2" diameter substrates, their surface was quite rough and had to be mechanically polished by hand at e2P. While the lower Sn content commercial grade 89/11 substrates were relatively straightforward to polish, the higher Sn content R&D grade proved quite difficult as the pits/pores and poor Sn mixing seemed to permeate throughout the sample regardless of the amount of material removed from the surface. This turned out to be quite unfortunate as the samples that proved easiest to mechanically polish also turned out to have a too low starting Sn content that resulted in the lowest T_c's. After mechanical polishing at e2P, the substrates were then sent to JLAB for electro-polishing. After electro-polishing the samples were ultrasonically cleaned, rinsed with ultra-pure water, dried in ISO6 cleanroom, and placed in the ECR chamber at JLAB. During the ECR deposition, the bronze substrates were not independently heated, with the only heating stemming from the incident ions of the ECR sputtering process. In-Situ substrate heating is a processing variable that needs further investigation. During Nb film deposition, two different bias voltages

were studied: -60 V and -120 V. Our target Nb film thickness was ~ 1 µm. After Nb film deposition, some of the samples were sent back to e2P and some remained at JLAB. A selected few of the JLAB Nb coated samples were analyzed using SEM/EDX. Others were loaded into their vacuum furnace for post reaction heat treatment. The Nb coated samples that were sent to e2P underwent a T_c measurement and then were loaded into a post reaction heat treatment in an inert Ar atmosphere. After heat treatment, samples once again underwent T_c testing. Two of the vacuum heat-treated samples underwent RF testing at JLAB.

The post reaction heat treatment regimens are another R&D area that needs significant optimization. As mentioned, the technical literature provided little guidance for an optimized post reaction heat treatment regimen that optimized Meissner state RF properties. Furthermore, the short duration of the investigation did not allow for long protracted heat treatments. In this study, time durations were in general limited to < 48 hours from start to finish and reaction temperature to a single uniform temperature in the range of 700-800°C (see Table I). Temperatures higher than 800°C were attempted on one run; however, since multiples samples of varying Sn content substrates were being reacted in a single chamber, partial melting of the 81%Cu/19%Sn sample resulting in contamination of all the samples which had to be discarded.

C. *Measurement and Analysis*

Time and fiscal restraints of the effort limited the types of testing and analysis that could be performed. All post reacted samples of reasonable visual quality (i.e. no flaking/peeling) were initially tested for its T_c using an AC inductance technique. Up to five (5) samples could be loaded onto a specially designed sample holder which was attached to the 2nd stage of GM cryocooler. To initially calibrate the T_c measurement apparatus, AC inductance measurements were taken as a function of temperature using pure Pb, pure Nb, and 2G YBCO thin films all of similar thicknesses (~ 1-3 µm). The samples T_c, defined here as its onset temperature, its transition width (ΔT_c), and diamagnetic response via its change in inductance value ($\Delta L = L_f - L_i$) were used to characterize the three calibration samples. To characterize the temperature lag between the Cernox® sensor and sample itself, measurements were taken both on cooldown (i.e. decreasing T) and warm-up (i.e. increasing T) and subsequently averaged. The pure Pb and Nb thin films showed a T_c onset within ~0.2 K of the literature value and the 2G YBCO film had an onset T_c ~ 91 K. All three calibration samples had a transition width ΔT_c < 1 K, and an inductance change ΔL ~ 25 µH. The manufactures stated accuracy of the Cernox® sensor was ~ 0.5 K.

III. TEST RESULTS

A. *AC Inductance Measurements*

Once the AC inductance measurement technique was verified and calibrated, tests were then performed on the smaller 10x10 mm heat treated Nb_3Sn samples. Fig 3 shows a typical diamagnetic response from a 86%Cu: 14%Sn 10x10mm sample. The two red, dashed lines demark the temperature transition width (ΔT_c). Both the initial cooldown (decreasing T) and warm-up (increasing T) measurements were used to determine if there was a "lag" between sample temperature measurement and actual sample temperature. The difference in T_c onset between initial cool-down and warm-up measurements was typically < 0.5 K.

In addition to the 'primary transition,' the majority of the results (not all) showed a substantial 'tail' in the transition

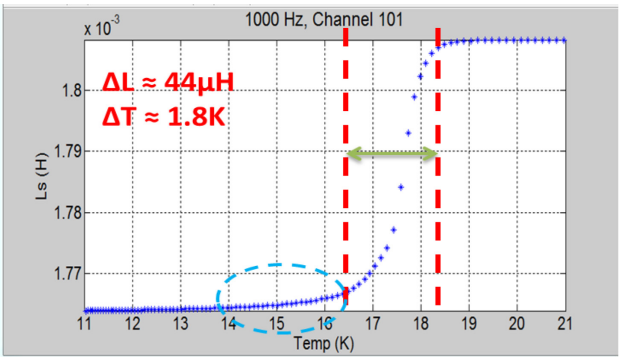

Fig. 3. Diamagnetic response of a 86%Cu/14%Sn 10x10 mm sample with T_c ~ 18 K, ΔT_c ~ 1.8 K, and ΔL ~ 44 µH.

width (see blue dashed circle). While we believe that this could be an indication of some non-stoichiometric low Sn content from the reaction diffusion process, this long tail was also observed in all of the pure ECR deposited Nb films prior to heat treatment, albeit at lower temperatures (~ 4→ 6 K). Some samples showed a smaller secondary transition at T_c ~ 9 K (not observed for sample shown in Fig. 3) indicating that a portion of the pure Nb film was not converted to the Nb_3Sn phase. The Nb film thickness is obviously another variable that requires further optimization in this modified BR process.

Interestingly, the magnitude of the diamagnetic response for many of the higher quality (i.e. higher final at wt. Sn content per EDX analysis) heat treated Nb_3Sn films showed a ΔL ~ 30-45 µH, when compared to the ΔL ~ 25 µH for the three calibration thin films. While there are several possible reasons for this larger diamagnetic response in the heat treated Nb_3Sn samples, one possible explanation could be that the reaction diffusion process may be converting a larger volume fraction of material to the superconducting Nb_3Sn phase than just at the initial surface of the ~ 1µm Nb film surface. A summary of the AC susceptibility test results for the 10mm x 10mm samples is shown in Table I. In general, test results were quite encouraging yielding T_c onset values ranging from ~ 15 K→18.3K with reasonably sharp transition widths ΔT < 2 K for many of the samples. For the highest quality Nb_3Sn samples, (i.e. those with the highest net post reacted at. wt. % Sn content), transition widths were extremely sharp with ΔT< 1 K. We are particularly encouraged by these promising results especially in light of the very short time duration of the study and the entirely new fabrication melt casted process.

TABLE I: Summary of Properties on 10x10 mm samples

Bronze	Sample Name	Nucleation Voltage (V) / Ion Energy (eV)	Heat Treatment	Soak Temperature (C)	Tc / Transition Width ΔT (K)	Inductive Signal Strength ΔL (μH)
C907 Cu/Sn: 89/11	907-1	-120/184	HT1	700	NA	NA
	907-2	-60/124	HT4	759	15.2/1.3	23 + 7
	907-3	0/64	HT6	798	14.8/1	8
	907-4	-240/304				
C909 Cu/Sn: 87/13	909-1	-120/184	HT1	700	NA	NA
	909-2	-60/124	HT4	759	17.3/1	30 + 7
	909-3	0/64	HT6	798*	17.6/1.3	33 + 10
	909-4	-240/304				
C910 Cu/Sn: 85/15	910-1	-120/184	HT1	700	18.3/0.8	0.35 + 0.2
	910-2	-60/124	HT4	759	18.1/1.3	29 + 7
	910-3	0/64	HT6	798*	16.9/1.6	21 + 10
	910-4	-240/304				
C911 Cu/Sn: 84/16	911-1	-120/184	HT2	700	17.5/1.4	35 + 8
	911-2	-60/124	HT5	700	16.2/1.2	32 + 3
	911-3	0/64	HT7	759	15.8/0.9	17 + 10
	911-4	-240/304				
C913 Cu/Sn: 81/19	913-1	-120/184	HT3	700	16.6/0.9	28 + 15
	913-2	-60/124	HT7	759	15.5/1.7	31 + 4
	913-3	0/64	HT7	759	16.0/1.4	26 + 4
	913-4	-240/304				

*Soak temperature seemed to be too hot for these samples: they appeared slightly melted after heat treatment

B. *SEM/EDX Analysis*

A select few of the pre and post heat treated samples underwent SEM/EDX analysis at JLAB (see Fig. 4). Shown in Fig. 4 is a series of SEM photographs on a 2" diameter 907 (i.e. 89% Cu/11% Sn) coupon heat treated for 24hr at 700°C in vacuum. EDX analysis of the surface reveals two interesting features. First, the small (~5μm) grains on the surface of the sample are Cu rich precipitates. Second, the smooth regions containing no Cu-rich precipitates show an under stoichiometric Sn content of ~15% relative to the desired 25% for optimal RF properties. The lower values of T_c are most likely due to lower than ideal post reacted at wt. % Sn content for under stoichiometric Nb_3Sn.[12] Although more SEM/EDX data is needed to confirm this hypothesis, the select few samples in which SEM/EDX measurements were taken show post reacted Sn contents varying between 8% and 24% (with ideal =25%), with the majority of the lower T_c samples resulting from the commercial grade 89% Cu/11% Sn ingot, which had the lowest starting Sn content of the bronze substrates. We caution the reader of the potential for confusion regarding the initial starting Sn % content of the starting bronze ingot compared to the final post reacted at. % Sn of the Nb_3Sn as measured by EDX.

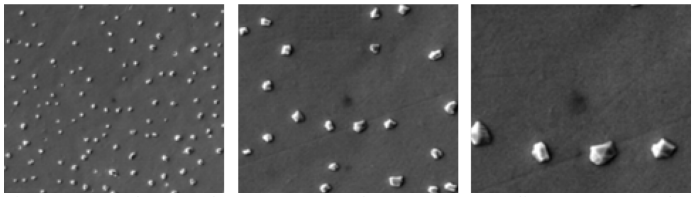

Fig. 4: SEM photographs at 50, 20, and 10μm on a 2" diameter 907 (89/11 Cu/Sn) coupon post 700°C vacuum furnace heat treatment

C. *RF Measurements*

Two vacuum heat-treated 89%Cu/11%Sn samples were further tested for RF surface resistance (R_s) and Q at JLAB. These RF measurements required a 2" diameter substrate (i.e. not the 10x10 mm) and were performed at 7.4 GHz using a calorimetric technique developed at JLAB.[13] These RF measurements showed two transitions at about 8 K and 14 K, with values of R_s about at least two orders of magnitude higher than similar high quality Nb_3Sn films directly deposited substrates by JLAB. This corresponds reasonably well with the poor performance observed in the AC inductance measurements of T_c. As a reminder, the commercial grade 89%Cu:11%Sn samples were initially selected for RF evaluation based upon their relative ease to mechanically polish and not its T_c value. It is unfortunate that time and funds of the investigation were exhausted before 2" diameter samples (required for RF measurements) with starting Sn contents > 87%Cu/13%Sn were fabricated, since their T_c, ΔT_c, and ΔL properties on the 10x10 mm squares were superior (see Table I). It would be interesting to see the relative effect on R_s and Q values, when comparing lower starting Sn content with superior surface finish to higher starting Sn content with inferior surface finish.

IV. Summary

While this initial investigation did demonstrate technical viability of the melt casting approach to some degree, there are several areas that need to be addressed in future R&D investigation in order to realize substantial improvements in RF performance. The first two steps in our BR fabrication process that did go quite smoothly. The 3D printed sand molds used in the melt casting proved to be relatively straight forward. This step was simple, quick, and low cost. In future R&D investigations, direct 3D printing of the metal matrix with subsequent "bronze infusion" will also be investigated. The bronze melt casting also proved to be relatively straight forward once the starting ingots were obtained. Future R&D investigation will require higher quality, void free, homogenous ingots with Cu/Sn ratios > 87/13. In addition, better electro-polishing methods and optimized heat treatment regimens are needed for correct stoichiometric Nb_3Sn phase formation.

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