

Results on Mono Element Internal Tin Nb₃Sn Conductors (MEIT) With Nb7.5Ta and Nb(1Zr + O_x) Filaments

Bruce A. Zeitlin, Eric Gregory, Jud Marte, Mark Benz, Tae Pyon, Ron Scanlan, and Dan Dieterich

Abstract—Results on high current density high volume fraction Nb7.5Ta MEIT conductor incorporating a Sn + Ti source with a J_c of more than of 3000 A/mm² at 12 T are presented and compared to a MEIT conductor incorporating Ti in the Sn. The effect of two fins on the D_{eff} and magnetization are discussed. Results on moderate volume fraction MEIT conductors with Nb1Zr filaments both with and without the addition of Oxygen are presented. The effect of oxygen on J_c , grain size and layer J_c are presented and discussed.

Index Terms—Internal tin, Nb1Zr, niobium tin, superconductors.

I. INTRODUCTION

THE High Energy Physics community world wide continues to drive the development of high performance low cost superconductors for the next generation accelerators and upgrades to existing machines. The Large Hadron Collider (LHC) is nearing completion. Serious consideration is being given either to doubling the energy to 14 TeV or increasing the luminosity. Either upgrade will require high performance Nb₃Sn at magnetic fields of at least 15 T. Conductor performance objectives originally established for the US DOE program have essentially become an international goal. These goals are to have a non copper J_c of 3000 A/mm² at 12 T, with a J_c of greater than 1000 A/mm², an effective filament size of less than 40 micrometers, an average piece lengths greater than 10 000 meters at 0.3 mm to 1.0 mm and all with a cost of less than \$1.5/kA-m. Heat treatment times should be less than 400 hrs with a target of 50 hrs [1]. The favored conductor is based on internal tin.

The internal tin concept allows high volume fractions of Nb₃Sn to be produced resulting in a high J_c value. Not only

is the fraction of Nb₃Sn high but its inherent current density is superior to low tin fractions [2]. The actual process for internal tin varies from manufacturer to manufacturer and is still undergoing development. Still the process has achieved the program's goal of 3000 A/mm² at 12 T [3]. High current density conductors though essentially have all their filaments bridged through reaction making the achievement of a D_{eff} of less than 40 micrometers only possible through a large number of sub-elements [1].

The MEIT process as presently developed addresses not only the current density issue but D_{eff} and a scalable process that can produce long lengths [4]. The process uses one multifilament element of internal tin that can be fabricated in 305 mm diameter. The introduction of fins internal to the array is intended to reduce D_{eff} [5]. The process bonds all elements in the hot extrusion eliminating the risk to wire length and yield inherent in any cold bonding process. MEIT is intended to be used as a seven strand cable to build to the desired size in a Rutherford cable. It also is amenable to varying J_c by the introduction of pure copper strands.

Several methods to raise the J_c of the layer and hence the conductor are being explored through our SBIR grants. Previous work on MEIT indicated that the Ti introduced in the Sn core may not have fully incorporated itself into the Nb₃Sn thereby reducing the J_c [4]. The use of a Nb7.5Ta alloy filament along with Ti in the Sn core should eliminate this concern. Another alternative being explored in this work focuses on refining the grain size by the introduction of ZrO₂ as used in the GE tape process [6]. Work by Dieterich *et al.* using thin film deposition techniques which added Sc, Al₂O₃ showed high current density of 10 000 A/mm² at 12 T with grains of 20 to 25 nm [7].

II. EXPERIMENTAL PROGRAM

A. Nb7.5Ta Filaments—Design, Processing, and Heat Treatment

BAZ8 was designed with Nb7.5Ta filaments with a local area ratios of .82 of Nb to copper. Table I presents the key parameters of the design as well as BAZ6 which incorporates pure Nb filaments and two fins. BAZ7 is included as this billet had the best J_c of previous work. The copper clad hex element, 3.27 mm across the flat, was produced by co-drawing the copper and Nb7.5Ta rod supplied by Cabot Performance Metals. A wrap of 7 layers of 0.51 mm pure Nb sheet was used as the diffusion barrier. Two fins of Nb60Ta 1.52 mm thick were introduced into the assembly. The clad hexes (#1027) were assembled in a 178 mm

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B. A. Zeitlin is with Supergenics LLC, Sarasota, FL 34242 USA (e-mail: brucezeitlin@comcast.net).

E. Gregory is with Supergenics I LLC, Jefferson, MA 01522 USA (e-mail: ericgregory@charter.net).

J. Marte is with GE Corporate Research and Development, Schenectady, NY 12301 USA (e-mail: marte@crd.ge.com).

M. Benz is with Engineering Horizons International LLC, Lincoln, VT 05443 USA (e-mail: benz@engineeringhorizons.com).

T. Pyon is with Outokumpu A. S. Inc, Waterbury, CT 06704 USA (e-mail: tae.pyon@outokumpu.com).

R. Scanlan and D. Dieterich are with the Lawrence Berkeley National Laboratory, Berkeley, CA 94720 USA (e-mail: rmscanlan@lbl.gov; drdieterich@lbl.gov).

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TABLE I
BILLET DESIGN COMPOSITION PARAMETERS

Billet	Nb at%	Sn at%	Cu at%	LAR	Nb/Sn
BAZ6	41.4	13.6	45.0	.73	3.04
#1095,Ti+Sn+2 fins					
BAZ8,#1027,Nb7.5	45.7	16.3	37.9	.82	2.8
Ta-2 fins					
BAZ7 #1044,Ti+Sn	39.1	15.6	45.3	.73	2.5

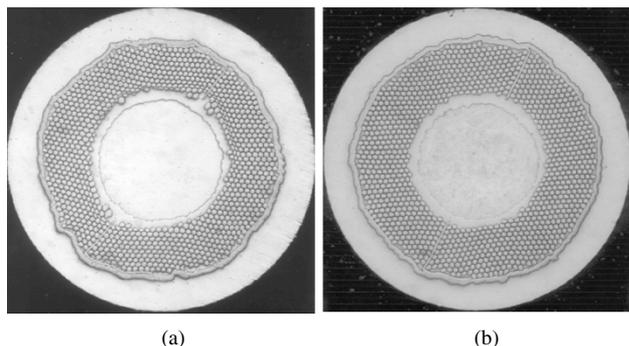


Fig. 1. (a) BAZ8 at 3.25 mm. (b) BAZ6 at 3.25 mm.

TABLE II
HEAT TREATMENT SCHEDULE

Billet	185 °C 10 °C/hr.	340 °C 10 °C/hr.	575 °C 50 °C/hr.	Final HT 50 °C/hr.
BAZ8	24 hrs.	48 hrs.		50,75,150 hrs. 675°C
BAZ7	24 hrs.	48 hrs.	100 hrs	150 hrs. 650°C

by 355 mm length billet which was evacuated, EB welded and hot isostatic pressed at 193–207 MPa for two hours at 600°C. The billet was extruded at 800°C to 37.6 mm at Nutech Precision Metals. Fig. 1(a) is a cross section of BAZ8 at 3.25 mm illustrating the barrier fins and somewhat irregular/sausaged filaments in the innermost row. Fig. 1(b) is BAZ6 with softer pure Nb filaments with undistorted inner filaments.

The billet was gun drilled and a Sn + Ti core inserted and drawn to 0.63 mm dia. wire at Outokumpu A.S. (OKAS) and then sent to NEEW in four pieces with the smallest 0.28 kg and the largest 8.04 kg. It was drawn on a variety of production machines before a final machine was chosen. Three to four breaks are probably associated with this optimization. Breakage also resulted from inclusions in the tin core of what was probably Yttria as Yttrium was detected in the x ray spectra of the inclusion. Samples of the wire were hand made into short cables of one active central strand with six copper strands. Cross sections indicated that the central strand wandered to the outside. The cable was heat treated in straight lengths by placing them in quartz or ceramic tubes. Table II gives the heat treatment regime.

B. Nb1Zr; Nb1Zr + 1Ti, Nb1Zr + 0

ZAB4 was designed to determine the effects of oxygen upon the performance of Nb1Zr filaments. The billet used annealed Nb1Zr rods of 2.44 mm dia. inserted into copper hex tubes 3.28 mm across the flats. The array of 258 filaments was stacked into a 88.9 mm dia. by 152.4 mm long billet which included a 6 layer diffusion barrier of 0.254 mm thick pure Nb sheet.

TABLE III
BILLET DESIGN PARAMETERS FOR ZAB4

Billet	Nb at%	Sn at%	Cu at%	Nb/Sn
ZAB4#258, Nb1Zr	25.4	12.1	62.5	2.06/1
After drawing				
Sn+SnO ₂ core	25.1	10.6	63.5	2.37/1

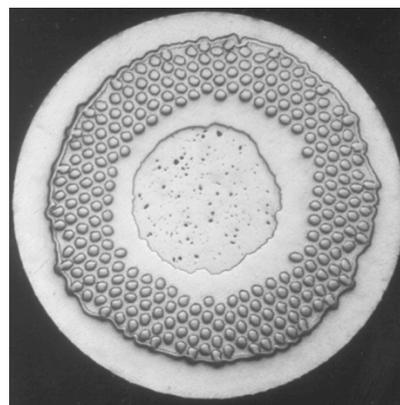


Fig. 2. ZAB4 with Sn + SnO core at 3.25 mm.

TABLE IV
ZAB4 HEAT TREATMENT MATRIX

Heat treatment	Sn+1Ti	Sn+Cu	Sn+SnO
700 °C /1 hr.	A1	A2	A3
700 °C /10 hr	B1	B2	B3
700 °C/100 hr.	F1	F2	F3
850 °C /1 hr.	D1	D2	D3
850 °C/10 hr.	E1	E2	E3
1000 °C/1 hr.	G1	G2	G3

Table III gives the design parameters of ZAB4. The billet was EB welded, hot isostatic pressed at 800°C for 1 hr. at 207 MPa and then extruded at 450°C to 22.22 mm dia all at GE CR&D. The rod was then turned to 20.45 mm before gun drilling to 8.25 mm at Grover Gundrilling. The turned diameter was less than desired but necessary as the rod was not as straight as required for gun drilling. The resulting rod was annealed for 1 hr at 975°C which reduced the hardness in the Nb1Zr from a nominal 180 VDP/180gf to 140 VDP. Cores of Sn + Cu, Sn + 1Ti and Sn + SnO with were prepared, the first two as solids and the last as a compressed powder. Enough SnO₂ was introduced to fully oxidize the contained Zr. The rod was then drawn at OKAS with the first draw at 17.4% area reduction followed by two draws with a 30% reduction and then completed with a 20% draw schedule. Some breakage was encountered in the Sn+SnO cored sample. Fig. 2 is a cross section of the as drawn rod with Sn + SnO₂ at 3.25 mm.

Heat treatments were chosen to provide a wide range of conditions to determine the effect of the various cores on the reaction amounts, grain size and J_c on the Nb1Zr filaments. No attempt was made for optimization. Table IV presents the times and temperatures used. All samples were heat treated straight in an alumina tubes wrapped in Ta with a flowing high purity Ar atmosphere. The samples were ramped at 10°C/hr. to 185°C and held for 24 hr., ramped at 10°C/hr to 340°C, held for 24 hrs and then ramped at 50°C/hr. to final temperature.

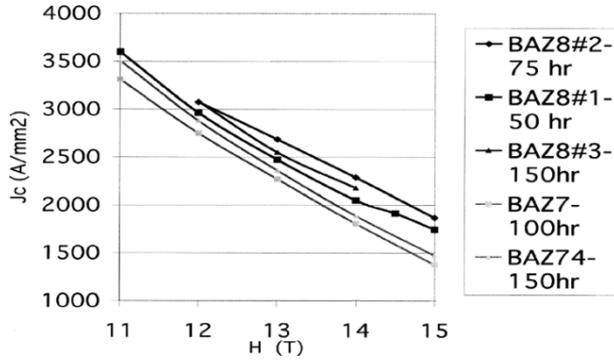


Fig. 3. J_c vs H for BAZ8 at 675°C, BAZ7 at 650°C.

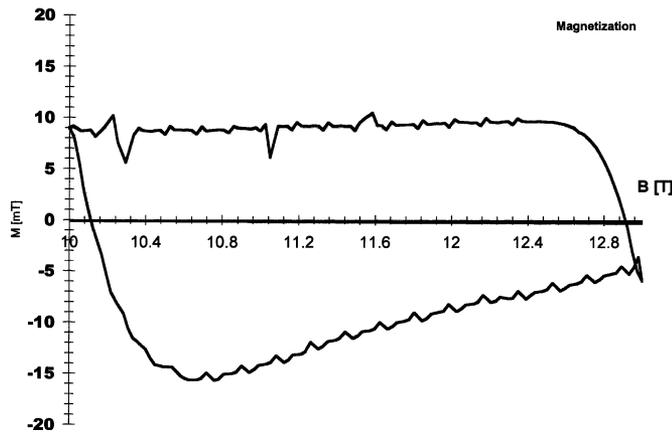


Fig. 4. Magnetization loop of BAZ8.

III. RESULTS

A. Nb7.5Ta Filaments

The BAZ8 samples were tested at Lawrence Berkeley National Laboratory in a 15 T superconducting magnet. The samples were mounted straight perpendicular to the field. The sample was about 31 mm long with 9.5 mm contact pads and potential leads about 5 mm apart. The holder allowed 4 samples to be tested at once. Fig. 3 presents the J_c for each heat treatment tested at an approximate 10^{-12} ohm cm sensitivity. The best values probably represent the sample more accurately as the small 0.154 mm wire is easy to damage. BAZ7 is presented for comparison but testing was done at NHMFL by R. Walsh on a standard ITER barrel resulting in a different strain condition.

Magnetization measurement as shown in Fig. 4 on BAZ8 were done at Fermi National Accelerator Laboratory by E. Barzi on a 0.254 mm strand heat treated for 75 hrs. at 675°C as described in Table II. An I_c of 56 amps at 15 T was measured at LBL and extrapolated to 95 amps at 12 T. D_{eff} calculated at 12 T is 127 micrometers with the actual physical core D_o including the barrier of 205 micrometers. The Sumption model for two splits would indicate $0.52 * D_o$ or 108 micrometers [8].

B. Nb1Zr Filaments

Samples from the heat treatment matrix in Table IV were examined by SEM to determine the amount of reaction and the grain size of the Nb_3Sn . GE CRD determined the area of reaction by measuring approximately 50 filaments. Fig. 5(a) & (b)

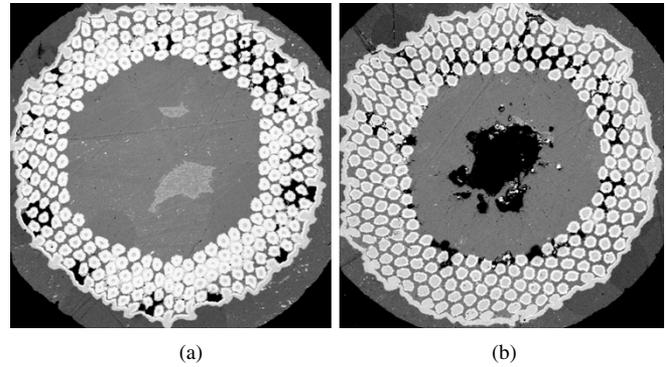
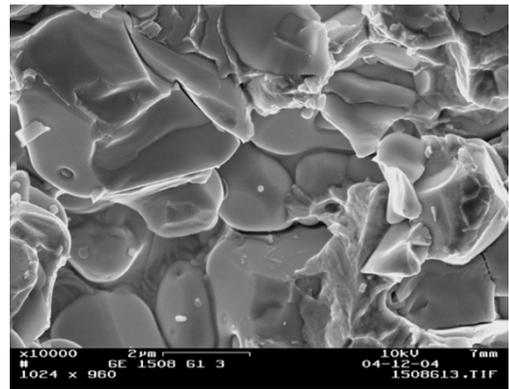
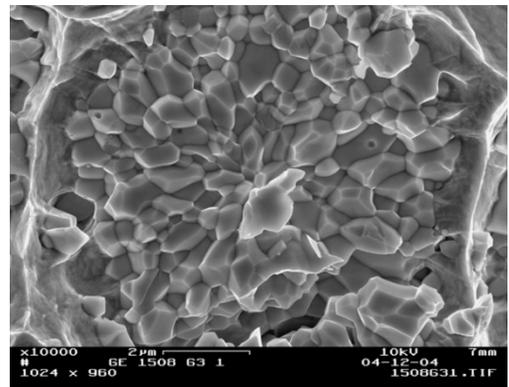


Fig. 5. (a) ZAB4 HT B1 Sn + Ti. (b) HT B3 Sn + SnO.



(a)



(b)

Fig. 6. (a) HT G1 Sn + Ti. (b) HT G3 Sn + SnO.

illustrates the reacted cross section of ZAB4 with (a) Sn+Ti and with (b) Sn + SnO for 10 hrs at 700°C. The grain size was the average equivalent round though it was only determined on one filament. The grain aspect ratios was typically in the range of 1.5–1.8 and seemed to be independent of the additive. Fig. 6(a) & (b) illustrates the difference between the samples grain size with and without SnO at 1000°C. Grain size differences between the additives are not very noticeable at lower temperatures. Table V gives a summary of the results.

The critical current density for the best samples of the Sn+Ti and Sn + SnO is given in Fig. 7. Quenching occurred for the Ti samples below 15 T in 2B1 and at all fields for F1 and E1. Fig. 8 compares the J_c vs H of the Sn + Cu to the Sn + SnO. The 1000°C samples had an H^* of about 10 T. Kurahashi, *et al.* reported a sharp drop in T_c and B_{c2} in bronze matrix conductors

TABLE V
PERCENTAGE AREA REACTION AND GRAIN SIZE FOR ZAB4

Sample	Reaction % \pm 8%	Grain Size nm	Grain Size s.d
A1 Sn+Ti 700°C 1 hr	45	74	29
A2 Sn+Cu 700°C 1 hr	37	69	31
A3 Sn+O 700°C 1 hr	23	71	23
B1 Sn+Ti 700°C 10 hr	87	85	29
B2 Sn+Cu 700°C 10 hr	91	102	28
B3 Sn+O 700°C 10 hr	57	89	23
F1 Sn+Ti 700°C 100	100	184	68
F2 Sn+Cu 700°C 100	100	155	57
F3 Sn+O 700°C 100	84	188	71
D1 Sn+Ti 850°C 1 hr	100	298	134
D2 Sn+Cu 850°C 1 hr	100	210	110
D3 Sn+O 850°C 1 hr	93	412	163
E1 Sn+Ti 850°C 10 hr	100	463	218
E2 Sn+Cu 850°C 10	100	392	175
E3 Sn+O 850°C 10 hr	93	406	177
G1 Sn+Ti 1000°C 1hr	100	1651	715
G2 Sn+Cu 1000°C 1	100	943	427
G3 Sn+O 1000°C 1 hr	100	719	259

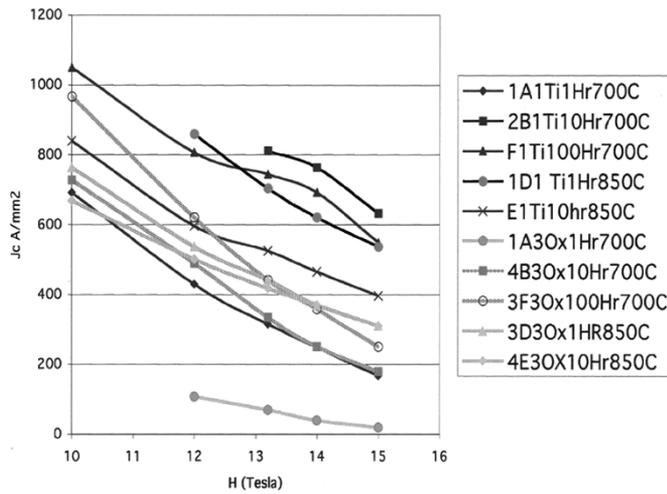


Fig. 7. J_c vs. H for Sn + Ti and Sn + SnO at various times and temperatures.

between a peak at 850°C and 940°C with Bc_2 at 940°C of 20 T [9]. One ternary of the system shows a solubility of 2 at.% of Cu at 1000°C though there is disagreement with other diagrams [10].

Layer current density, Fig. 9, at 12 T as a function of reaction temperature was calculated. J_c was extrapolated for the Ti samples for the 12 T values. Reaction of the barrier is not taken into account which could overstate the results by 5%.

IV. DISCUSSION

A. Nb7.5Ta

The non uniformity of the inner filaments after extrusion suggests that a lower temperature extrusion would better match the strength ratios of the components [6]. Breakage of BAZ8 was greater than BAZ6 and BAZ7. Larger and non uniform inner filaments, Ytria inclusions and the higher tensile and work hardening rate of the alloy all contributed. A total of 26 256 meters of 0.254 mm diameter wire was produced with the average length

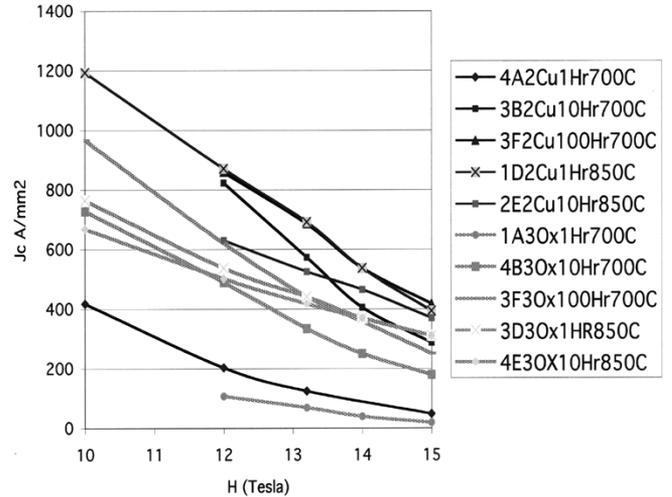


Fig. 8. J_c vs. H for Sn + Cu and Sn + SnO for various heat treatments.

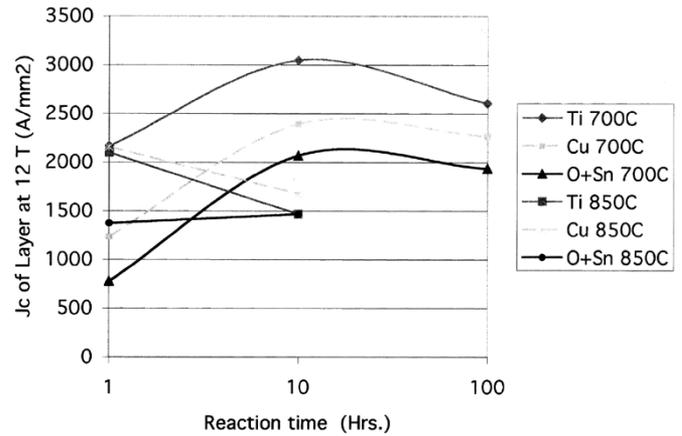
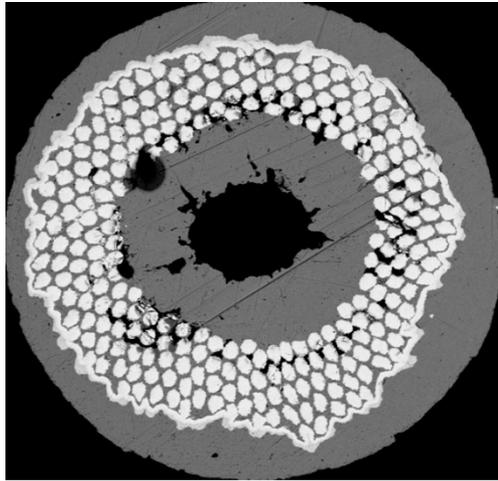


Fig. 9. Layer J_c at 12 T vs. time for ZAB4 with additives.

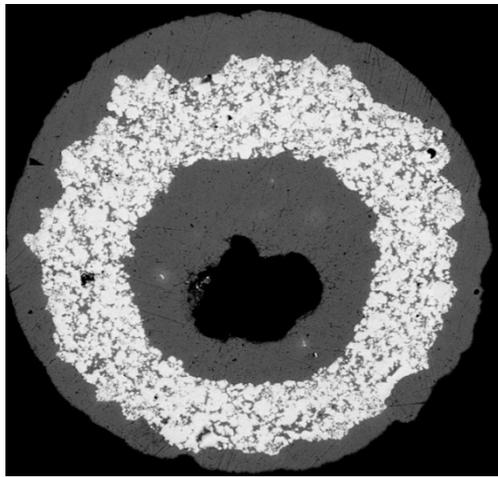
of 1544 meters and a median of 1069 meters. The longest piece was 5884 meters. Eighty four percent of the wire (7 pieces) was greater than 2051 meters. In contrast, BAZ6 had a mean length of 7373 meters, a median of 6673 meters with 80% of the wire (5 pcs.) greater than 6672 meters.

The non copper current density of BAZ8 was relatively insensitive to heat treatment time. Current density at 12 T normalized to the starting Nb plus the reacted portion of the barrier (40%) was 5940 A/mm² in BAZ8 vs. 6365 A/mm² in BAZ7. In the Nb₃Sn layer this corresponds to 4273 A/mm² and 4579 A/mm² respectively (39% expansion assumed). The cross over in current density occurs at about 14 T with BAZ8 superior at 15 T. The differences in testing technique, hence strain state and the fact that both have Ti in the Sn core make drawing any firm conclusions difficult. Increasing the Nb percentage to 45 at% though seems to be the key to meeting the programs goal at 12 T.

The fins do seem to be effective giving a reduction to 0.62 D_o though not as predicted by the model. Still the alloy is a weak superconductor and proximity effects may lead to reduced effectiveness. Fins using pure Ta and or a ferromagnetic material may be necessary [11].



(a)



(b)

Fig. 10. (a) G3 1 hr 1000°C. (b) G2 1 hr 1000°C.

B. Nb1Zr

The results in Table V indicate that the addition of the SnO reduced the rate of reaction by at least a factor of 10. The reduced available tin about 12% is not considered significant enough for this rate reduction. At 1000°C the non oxygen samples actually had the copper stabilizer melt as can be seen from the irregular shape of G2 in Fig. 10(b). This is probably related to the leakage of the barrier such that low melting bronze formed and melted. In contrast the SnO sample was fine with a normal cross section.

The grain size variation as seen in Table V also indicates that only at 1000°C was there a statistically significant difference between the compositions. The SnO was effective in controlling the grain size. The grain size of the non oxygen samples grew so large that the filaments essentially merged together in many locations as seen in Fig. 10(a), (b). Grain size of additional filaments have to be taken to lower the standard deviation (s.d.).

The layer current density as shown in Fig. 9 is best for comparing the samples and variations as the differences in reaction area is taken into account. Current density of the Ti bearing samples is best for the times studied. It appears that current densities at 700°C for the Sn + Cu and Sn + SnO samples are similar though reaction rates for the Sn + SnO are slower. At 850°C all

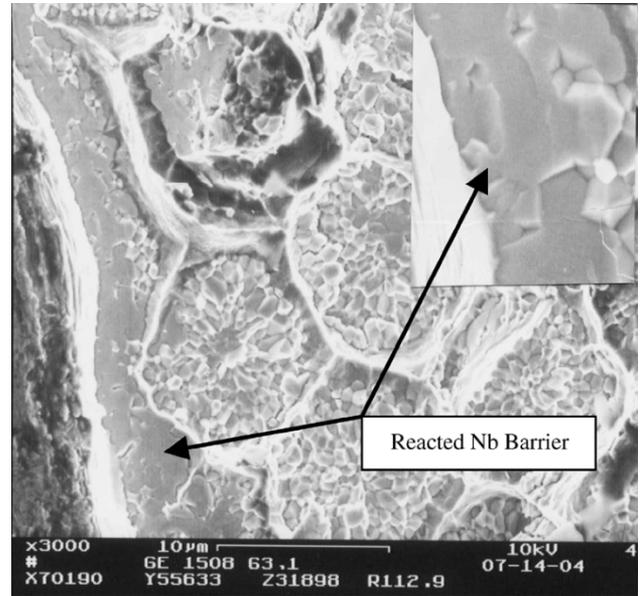


Fig. 11. Sample G3 Nb barrier and filaments at 3000X and 10000X.

values appear to be converging at 10 hrs. with the Ti projected to decrease while the slope of the Sn + SnO sample appears to be the flat giving some indication that after 10 hrs. its values would be superior. The best values of the non Ti samples layer current densities as compared to ITER conductors is similar with a 2400 A/mm² to 2000 A/mm² as compared to 1900–2400 [12].

The overall results would seem to indicate that the addition of Oxygen has little beneficial effects except at 1000°C but a number of issues still remain to be resolved. First we are uncertain how much ZrO₂ is needed to refine the grain structure. To that end we still have to measure how much oxygen was contained in the starting Sn and Sn + Ti. Examination of the Nb barrier, as seen in Fig. 11 shows significantly larger grains at the edge of the reacted barrier than the respective Nb1Zr filaments indicating Zr does have an effect. Diffusion calculations done for pure Cu and Nb indicate that the Oxygen should be in the filaments prior to reaction. These calculations do not take into account the effect of the tin hence we are not certain where and when the oxygen is during reaction. Future work using a Nb1ZrO_x alloy as well as further analysis should resolve this issue [6].

V. CONCLUSION

MEIT conductors using Nb7.5Ta filaments and internal barriers can achieve 3000 A/mm² and reduce D_{eff}. Piece length still can be improved but does hold the promise of meeting the HEP goals.

Nb1Zr with Oxygen introduced internally has not yet demonstrated its potential but has shown grain refining effects at high reaction temperatures. More work is in progress to better determine if direct introduction into the alloy will be more effective.

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