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RESEARCH AND DEVELOPMENT OF STABILIZED MULTIFILAMENTARY Nb_3Sn SUPERCONDUCTORS

Fred T. Ormand

JANUARY 1, 1976 through SEPTEMBER 30, 1976

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Technical Report for University of California
Lawrence Livermore Laboratory
Livermore, California

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On work performed under
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SUMMARY

The basic objectives of this work included: making additional test samples of 1 000A (at 12T) conductor, scaling up the production of 3 500A conductor to larger billets, and improving the performances of 1 000A size conductor by utilizing 13.5 wt % tin-bronze rather than 10% bronze.

Additional samples of 1 000A conductor were made successfully from a 51mm diameter third-stage billet. This 1.68 x 5.00mm conductor had a critical current of 1 060A at 12T, 4.2K and 10^{-13} Ω m.

A 101mm diameter third-stage billet of 3 500A configuration was extruded, drawn, and reacted successfully to make 3.12 x 9.40mm conductor. Current was 3 600A at 12T, 4.2K and 10^{-13} Ω m.

A 187mm diameter third-stage billet of 3 500A configuration, packed with hexes from two scaled-up 152mm diameter second-stage billets, was unsuccessful. Longitudinal cracks appeared in some portions of the second-stage extrusions during drawing. Multiple breaks were found in each of the tantalum barriers after drawing the third-stage extrusion. It is not yet clear whether these problems are attributable to impurities, or unfavorable metallurgical conditions in the tantalum or the bronze, or to scaling up to a larger size.

First, second and third-stage billets containing 13.5 wt % tin-bronze were extruded and drawn to appropriate sizes. The 1.68 x 5.00mm conductor was reacted to give a critical current of 1 800A at 12T, 4.2K and $10^{-13}\Omega$ m.

~~A paper based largely upon work done for LLL in FY 1975-1976 was given at the Applied Superconductivity Conference at Palo Alto, California. [1]~~

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1.1 1 000A Samples from 51mm dia. Billet: A 51mm diameter, 152mm hex length, third-stage billet was packed with 19 hexes drawn from a second-stage billet extruded in FY 1975 and held in inventory for LLL. The standard 1 000A configuration was used, $[19 \text{ x } \{(187 \text{ x } [19\text{Nb in } 10\%\text{Bz}])_{\text{Ta}}\}_{\text{Cu}}]_{\text{Cu}}$ with 34 area % copper.

Twenty test samples, each 1.68mm x 5.00mm x 1.2m long, were reacted and delivered to LLL. These consisted of one group of 10 samples (7 having a 50mm twist pitch and 3 having no twist) reacted 2 days at 650°C and a second similar group (7 twisted and 3 not twisted) reacted 4 days at 650°C. LLL reported 1 060A at 12T, 4.2K and $10^{-13}\,\Omega$ m [2] (neglecting the cross sectional area of Cu in calculating resistivity) for the 4 day samples, see Table I and Figures 1, 7 - 9. However these samples were reported to be less ductile at room temperature than some tested earlier, breaking at 1% elongation. This problem is discussed in Section III.

1.2 3 500A Conductor from a 101mm diameter Billet

A 101mm dia, 213mm hex length, third-stage billet was packed with 73 hexes drawn from second-stage billets extruded in FY 1975 and held in inventory for LLL. The standard 3 500A configuration, previously used only with 51mm dia billets,

$[73 \text{ x } \{(187 \text{ x } [19\text{Nb in } 10\%\text{Bz}])_{\text{Ta}}\}_{\text{Cu}}]_{\text{Cu}}$ with 34 area % Cu, was used.

Ten test samples, each 3.12mm x 9.40mm x 1.2m long were reacted 4 days at 650°C and delivered to LLL. Seven samples had a twist pitch of 100mm and 3 had no twist. LLL reported

3 600A at 12T, 4.2K and $10^{-13}\Omega$ m [2] (neglecting Cu in calculating resistivity) See Table I and Fig. 1, 7, 8. However these samples were also reported to break at 1% elongation at room temperature. This question is further discussed in Section III.

1.3 Scale-up to Larger Billets

A 152mm diameter second-stage billet was packed with 187 hexes drawn from a 187mm diameter first-stage billet (19Nb in 10% Bronze) extruded in FY 1975 and held in inventory for LLL. The seamless tantalum liner was fabricated from metallurgical grade, electron beam melted tantalum. The standard second-stage configuration was used.

$$\{(187 \times [19\mathrm{Nb\ in\ 10\%\ Bz}])_{\mathrm{Ta}}\}_{\mathrm{Cu}}$$

This billet was extruded to 38.18mm dia. and seemed perfect in cross-section. After annealing, the extrusion was drawn in 3 passes to 28.4mm dia. then annealed and drawn in 3 more passes to 20.9mm diameter and annealed. After examination, occasional lengthwise cracks and stretch marks were found on the surfaces of these rods. Cross-sectioning revealed cracks in the tantalum barrier which sometimes extended into the bronze matrix interior and sometimes broke through the copper shell. (Fig. 3). Only one crack existed at any one portion of the rod, but at times it disappeared and re-appeared some multiple of 60° around the rod.

Since this type of fracture has not been observed previously with 110mm diameter billets, a substantial effort was made to determine its cause. The following possible causes were considered:

A. Impurities or unfavorable metallurgical conditions in the tantalum liner resulting in embrittlement.
B. Impurities or unfavorable metallurgical conditions in the bronze leading to crack formation at the bronze-tantalum interface.
C. Inadequate cleaning, pickling, rinsing and/or drying of billet components before assembly.
D. Leaky electron beam welds in billet before extrusion, allowing air to leak into billet and contaminate tantalum during preheating before extrusion.
E. Abnormally rapid work hardening of the bronze matrix during drawing, suggesting a need for more frequent annealing.
F. Penetration of the nitrogen annealing atmosphere into the tantalum barrier layer. However this seemed unlikely with the copper jacket.
G. Some unsuspected effect of scale-up concentrated insupportable stresses in the barrier layer. In this case, however, the tantalum might be expected to yield or neck-down rather than crack.

Chemical analysis and metallurgical testing of samples of the tantalum stock used for the liners were generally within manufacturers specification, except for silicon and tungsten. See Table II. Unfortunately we do not have a sample of the tantalum used to make the original seamless liners for the successful 110mm diameter billets for comparison. These had been fabricated by the same firm from tantalum made by the same manufacturer to the same nominal specifications.

The first-stage billet had been extruded and drawn without difficulty and its bronze matrix had seemed to work harden at a normal rate.

A second 152mm diameter second-stage billet was assembled using a liner made from the same tantalum stock and packed with hexes from a first-stage billet made from the same bronze and niobium stock.

Extreme care was used in degreasing, pickling, rinsing and drying all billet components.

After assembly, the nose cone and lid were TIG welded in an argon-filled chamber. The billet was evacuated through a copper tube welded in the nose cone which was then crimped off and weldad to preserve the vacuum. After extrusion, the billet was annealed in an argon-atmosphere, drawn into two passes to 31.1mm dia., annealed in argon, drawn into two passes to 26.2mm dia. and annealed again. This billet cracked on drawing to 23.3mm.

In order to gain further information, and possibly produce some useful material, the rods produced were drawn to 17.9mm hex and packed in a third-stage billet, 187mm dia. 305mm hex length. The billet was extruded to 50.80mm dia., annealed, and drawn to 36.4mm diameter. A cross-section taken at 36.4mm dia. revealed multiple breaks at each barrier. (See Fig. 4)

So far, the most likely explanations for cracked second-stage rods appear to be:

A. Some material problem with the tantalum liners.

G. Some unidentified stress concentration due to mechanical or thermal effects in scaled-up billets and extrusions.

Explanation B, some material problem in the bronze, remains a possibility but seems less likely.

2. Conductors Utilizing Nb Filament in 13.5 wt % Tin Bronze.

2.1 First-Stage Billets. Two billets containing 19 niobium rods in a bronze matrix were fabricated from bronze ingots cast in our vacuum induction melting (VIM) furnace. The bronze melt composition was 14 wt % tin (Pass 1, 99.95%) and 86 wt % OFHC copper. Analyses of samples taken from the ingots indicated 13.5 wt % tin, suggesting either vaporization of tin or slight analytical error.

Three 22 kg ingots were cast. After a homogenization heat treatment, they were machined and drilled to produce two 19 hole billets and one solid billet for filler stock, all 110mm diameter. The 19 hole billets were loaded with 118mm long Nb rods and the lids were electron beam welded in a vacuum chamber. All three billets were extruded to 28.58mm diameter rods. The two 19 filament extrusions were 28.4 area % Nb.

2.2 Second-Stage Billet. A 110mm diameter, 203mm hex length billet was packed with 283 hexes drawn from the 19 filament first-stage billet described above. The solid filler stock was used to circularize the assembly inside the tantalum liner. The seamless tantalum liner dimensions were 103 mm OD, 1.59mm wall. The configuration used was: $\{ (\text{[illegible]} \times [19\text{Nb in } 13.5\%\text{Bz}]])_{\text{Ta}}\}_{\text{Cu}}$ This billet was extruded to 28.6 mm dia. The composition of the extruded rod is given in Table I. The bronze to Niobium ratio was 2.89:1.

A portion of this extrusion was drawn to 0.67mm diameter and 0.55mm diameter wires for determining heat treatment times and temperatures. (See Fig. 5, 9). A maximum current density of 770 A/mm^2 at 4.2K, 10T, and 10^{-12} Ω m was obtained in the Nb$_3$Sn-Nb-Bronze composite. (See Table I and Fig. 9)

Another portion of this extrusion was drawn to hex cross-section for packing a 76mm diameter third-stage billet.

This second-stage billet drew satisfactorily with no evidence of cracking. These composite rods and wires were annealed after every 50% reduction in area.

2.3 Third-Stage Billet. A 75.7mm diameter, 152mm hex length, billet was packed with 19 hexes from the previous second-stage billet (with Cu fillers to circularize the assembly inside the Cu can). The configuration was:

$[19 \times \{ (283 \times [19\text{Nb in } 13.5\%\text{Bz}])_{\text{Ta}} \}_{\text{Cu}}]_{\text{Cu}}$

The billet was extruded to 19.7mm diameter. This 102 163 filament extrusion contained 34 area % Cu. Composition details are given in Table I.

The extruded rod was drawn to 4.11mm diameter wire, 20.6% reduction per draw, annealing every 3 draws. One portion of this wire was twisted, "turk's head" rolled and rectangular die drawn to 1.68 x 5.00mm with a 50mm twist pitch. Another portion was processed similarly without twisting. 7 twisted samples 1.2m long and 3 not-twisted samples were reacted in straight grooves in a graphite form for 72 hours at 700°C. These samples were shipped to LLL for testing and evaluation. LLL reported [2] a critical current of 1 800A at 4.2K, 12T and $10^{-13}\Omega$ m. (See Table I and Fig. 6-8). The ductility of this conductor has been reported by LLL to be quite low, it broke in a room temperature tensile test at 0.7% strain.

This suggests that at the higher percentage of Nb_3Sn formed in the conductor designed for 13.5 wt % Sn-bronze, the entire conductor breaks when the Nb_3Sn layers break. Earlier test data by LLL suggested a maximum safe strain of about 0.6% before degradation of I_c due to damage to Nb_3Sn layers.

3. Variation of Ductility of Nb_3Sn Superconductors.

3.1 **Conductor Utilizing 13.5wt % Sn Bronze.** It seems likely that the low ductility of the conductor utilizing 13.5wt % Sn-Bronze can be attributed to the high percentage of Nb_3Sn formed in the conductor. Although it is extremely difficult to obtain an accurate measure of the quantity of Nb_3Sn formed, this conductor was designed around the estimate that 80% of the Nb in each filament would be reacted. Larbalestier, et. al [3] have estimated a volume increase of 37.5% during the conversion of Nb to stoichiometric Nb_3Sn. Since there is no large increase in conductor length during reaction, this increase must result in a 37.5% increase in cross-sectional area of reacted Nb forming Nb_3Sn. So if 80% of the Nb in each filament reacts, the cross-sectional area of Nb_3Sn formed is 1.375 x 80% of the initial Nb filament area. So the final area of Nb_3Sn is estimated to be 110% of the initial Nb area, and the final total filament area to be 110% Nb_3Sn + 20% Nb or 130% of the initial filament area. In principle, increases in the total filament volume should be compensated by decreases in matrix volume due to deplition of Sn in the bronze. However, the formation of Kirkendall porosity in the bronze matrix prevents exact compensation.

The original Nb + Bronze regions of the conductor are 25.6 area % Nb before reaction and (neglecting changes in total conductor volume) approximately 28.2 area % Nb_3Sn after reaction. The overall conductor is 15.9 area % Nb before reaction and (neglecting changes in total volume) 17.5 area % Nb_3Sn after reaction.

3.2 Conductors Utilizing 10 wt % Sn Bronze

Applying a similar analysis to the conductor design used for 10% Bronze gives the following estimates: 70% of the Nb in each filament converted, final area of Nb_3Sn = 1.375 x 70% = 96.25% of initial area of Nb. Neglecting changes in total conductor volume, as before, leads to the following estimate:

The original Nb + Bronze regions were 20.8 vol % Nb before reaction and about 20.0 vol % Nb_3Sn after reaction. The overall conductor was 12.9 vol % Nb before reaction and at most about 12.4 vol % Nb_3Sn after reaction.

Earlier conductors (FY 74 and FY 75) were relatively ductile, breaking at 10 to 25% elongation (except for samples of 3.5 kA conductor drawn to 1 kA size). However, bend test data indicated break up of Nb_3Sn and loss of superconducting continuity beyond a safe bending strain of 0.62%. Third-stage conductors completed in FY 76 had rather low ductilities, breaking at about 1% elongation. Since the first-stage, second-stage, and third-stage (before reaction) rod and wire stock could be drawn without unusual difficulty, it seems that ductility was lowered during the final high-temperature reaction forming Nb_3Sn. It is possible that the quantity of Nb_3Sn formed in these conductors is borderline with respect to ductile composite behavior. If so, small variations in mechanical properties may determine whether maximum elongation of the entire composite falls near that of Nb_3Sn or that of the other materials present.

The only known differences between the high and low ductility composites are the methods of preparing the bronze for the first stage extrusion, the diameters of the first stage extrusions, and the twist pitch in the finished conductors.

For conductors found to be ductile, the first-stage billets were 110mm diameter and were made from bronze stock prepared in either of two ways:

Some first-stage billets were machined and drilled from 10% tin-bronze ingots vacuum induction melted (VIM) in our laboratory and cast in graphite molds.

Others were machined and drilled from solid 10% bronze extrusions. These were VIM melted and cast in 267mm diameter graphite molds, machined to 251mm diameter solid billets, preheated in a salt bath and extruded to 113mm diameter.

Conductors having low ductility after reaction were made, at least in part, from first extrusion billets 178mm dia. Bronze ingots were VIM melted and cast in 267mm ID graphite molds. The ingots were forged to a larger diameter and extruded to 184mm diameter billet stock.

The more ductile 1 000A conductor samples delivered in 1975 had a twist pitch of 33mm, while the less ductile 1 000A samples delivered in 1976 had a twist pitch of 50mm.

Since our intermediate anneals at 500°C do not anneal the Nb filaments, conductors made from larger diameter first-stage extrusions must have more cold-work in the filaments than conductors having the same diameter filaments but made from smaller diameter first-stage extrusions. Hot working the bronze castings in air may have increased their oxygen content. The longer twist of the recent material may provide less "spring action" under elongation. These effects may be sufficient to determine whether the entire composite breaks near the same strain as the Nb_3Sn or at a considerably higher strain.

3.3 Discussion.

The variation of ductility in similar composites based on 10 wt % tin bronze may be governed by cold work in the Nb filaments, by the concentration of oxygen in the bronze or by the twist of the completed conductor. The quantity of Nb_3Sn formed may be so near to the borderline of ductile composite behavior that very minor chemical and/or metallurgical differences may be important.

The low ductility of the conductors based on 13.5 wt % Sn Bronze may be inherent in conductors containing over 25% Nb_3Sn in the Nb_3Sn + Nb + Bronze regions.

In a practical sense, the most significant consideration is the strain at which degradation of the critical current in Nb_3Sn begins, and especially the strain at which irreversible degradation occurs. It is extremely important to determine whether any combination of filament configuration, matrix composition, and reaction conditions can improve the effective ductility of the Nb_3Sn layers without sacrificing overall critical current density.

If design considerations require structural integrity beyond the strain at which superconducting continuity is destroyed, some sacrifice of current density may be required. Conductors containing a smaller fraction of Nb_3Sn with a higher J_c in the reaction layers will probably offer the best compromise between overall J_c and ductility.

References

(1) E. Adam, E. Gregory, and F.T. Ormand "Further Developments in Stabilized Multifilamentary Nb_3Sn Superconductors". Presented at the <u>1976 Applied Superconductivity Conference</u>, Stanford University, Palo Alto, California, August 17 - 20, 1976

(2) J. P. Zbasnik (private communications)

(3) D.C. Larbalestier, P.E. Madsen, J.A. Lee, M.N. Wilson, and J.P. Charlesworth. "Multifilamentary Niobium Tin Magnet Conductors" <u>IEEE Transactions on Magnetics</u>, vol. MAG-11, no. 2, pp. 247-250, March 1975.

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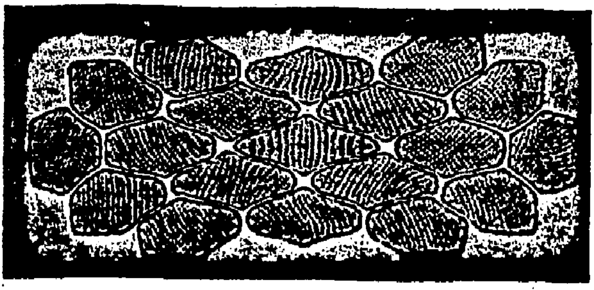

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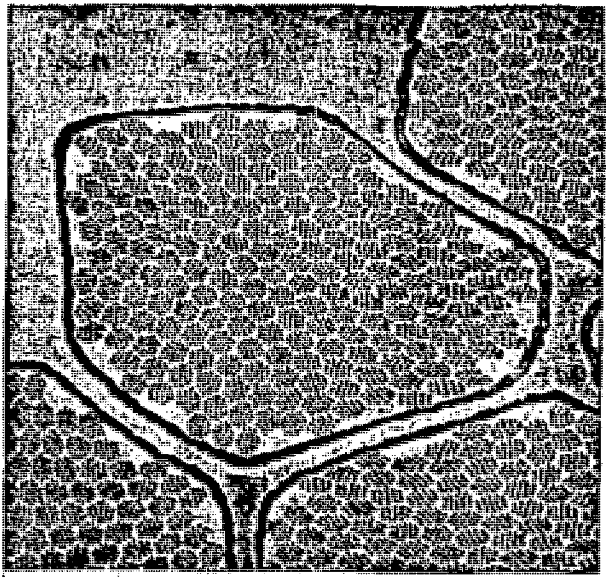
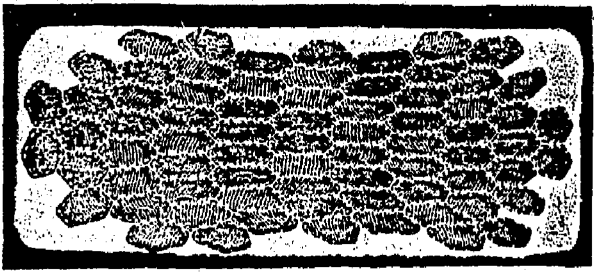


100X

Figure 1

19-Module Conductor Utilizing 10% Sn - Bronze (1.68 x 5.00 mm)



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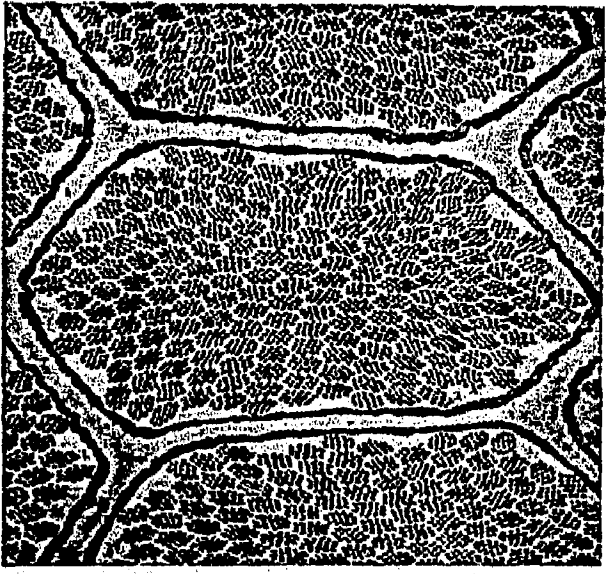


100X

Figure 2

73-Module Conductor Utilizing 10% Sn Bronze (3.12 x 9.40 mm)

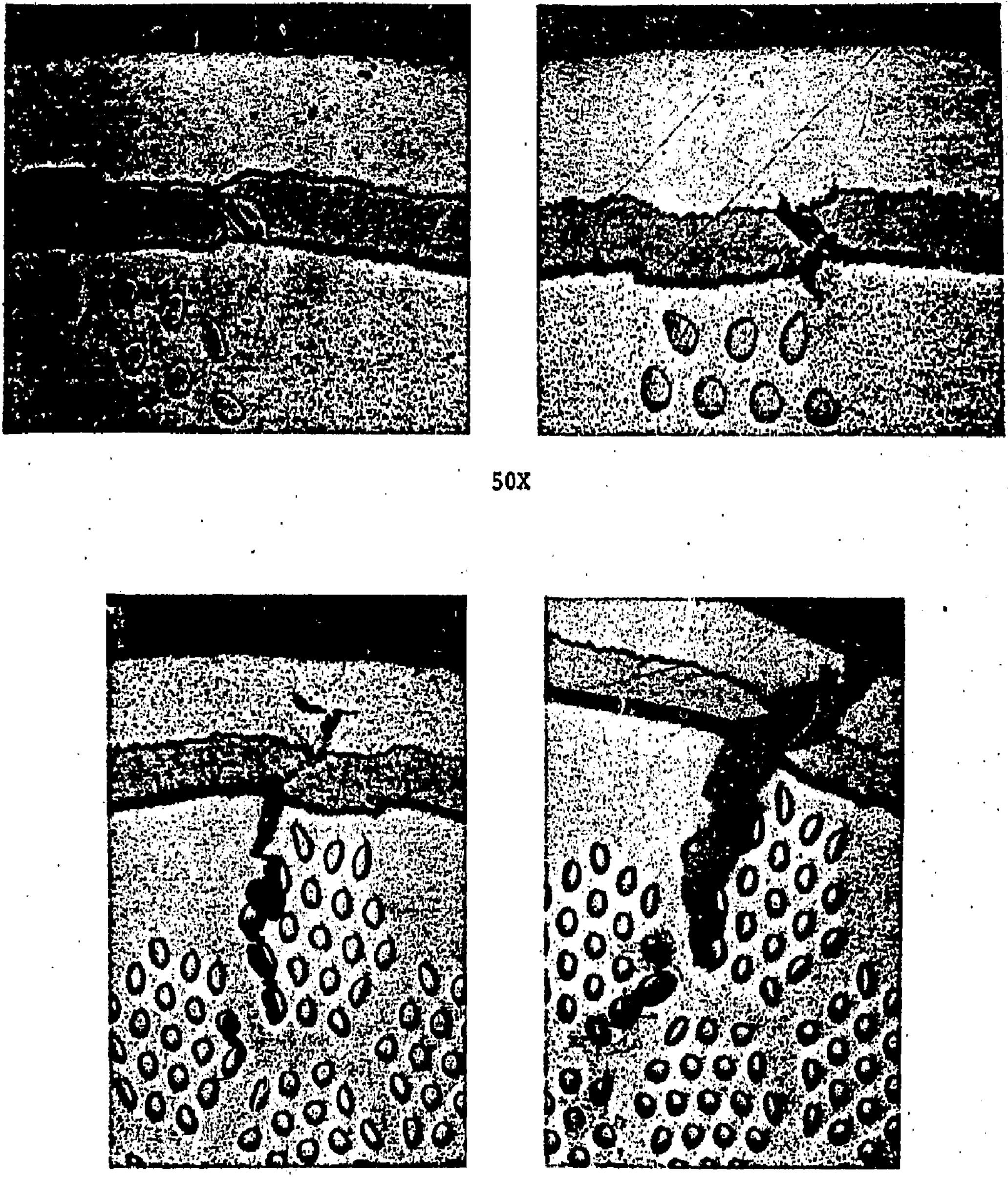
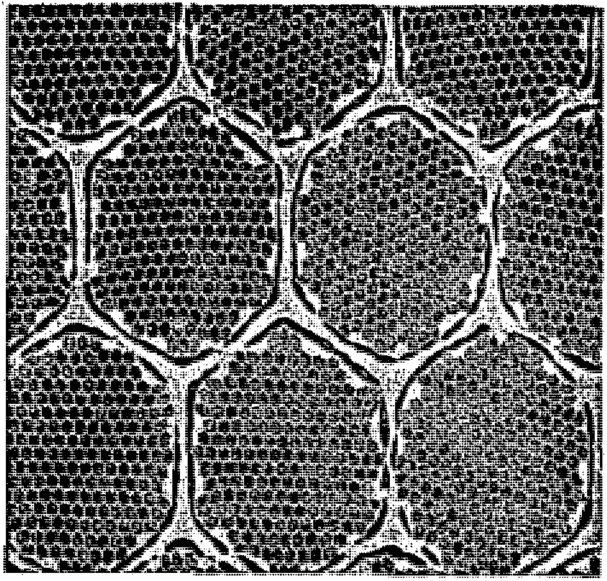


Figure 3

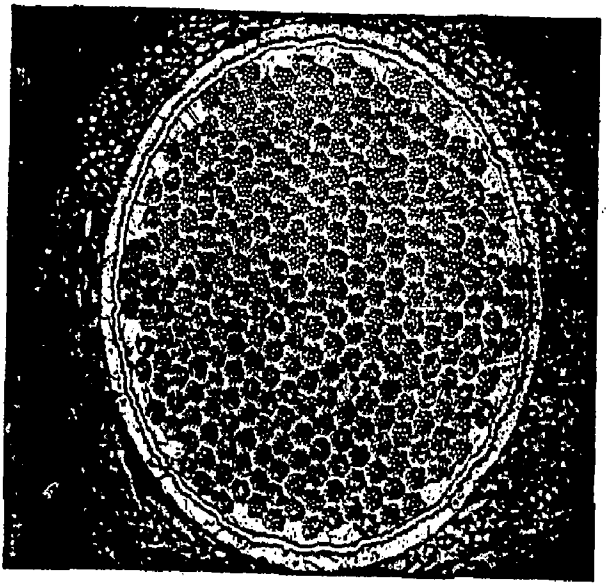
Various Stages of Cracking in Rod (20.85mm dia.) Drawn From Extrusion from 152mm dia. Second Stage Billet.



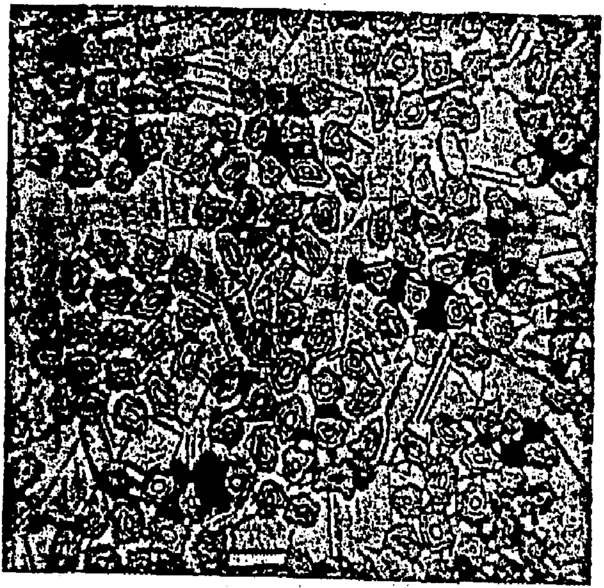
12.5X

Figure 4

Multiple Breaks in Ta Barriers in Rod (36mm dia)
Drawn from Extrusion from 187mm dia 73-Module Billet.



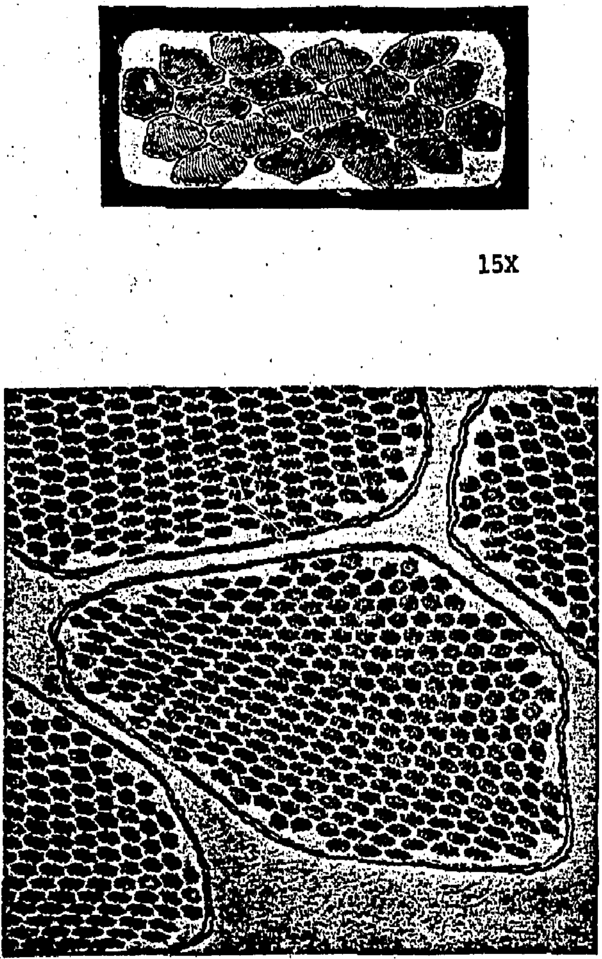
110X



1200X

Figure 5

1-Module Conductor Utilizing 13.5% Sn-Bronze (0.686mm dia)



15X

125X

Figure 6

19-Module Conductor Utilizing 13.5% Sn-Bronze (1.68 x 5.00 mm)

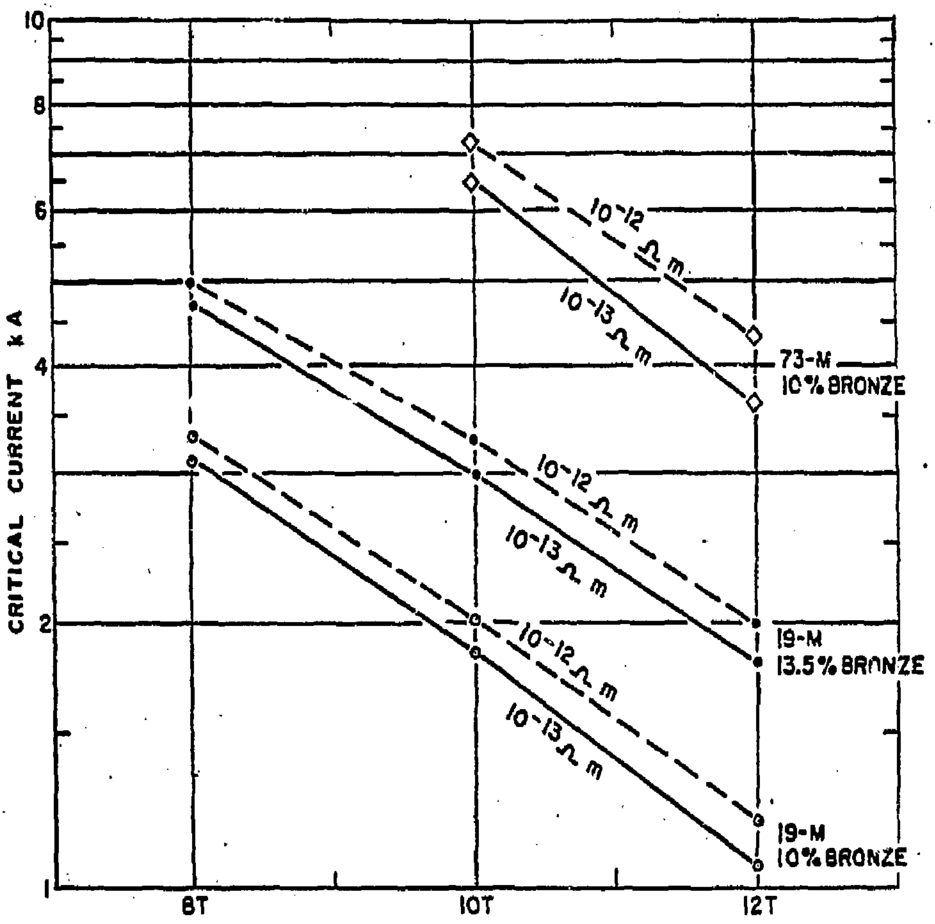


FIGURE 7.

CRITCAL CURRENT vs. MAGNETIC FIELD AT 4.2K FOR THIRD-STAGE CONDUCTORS.

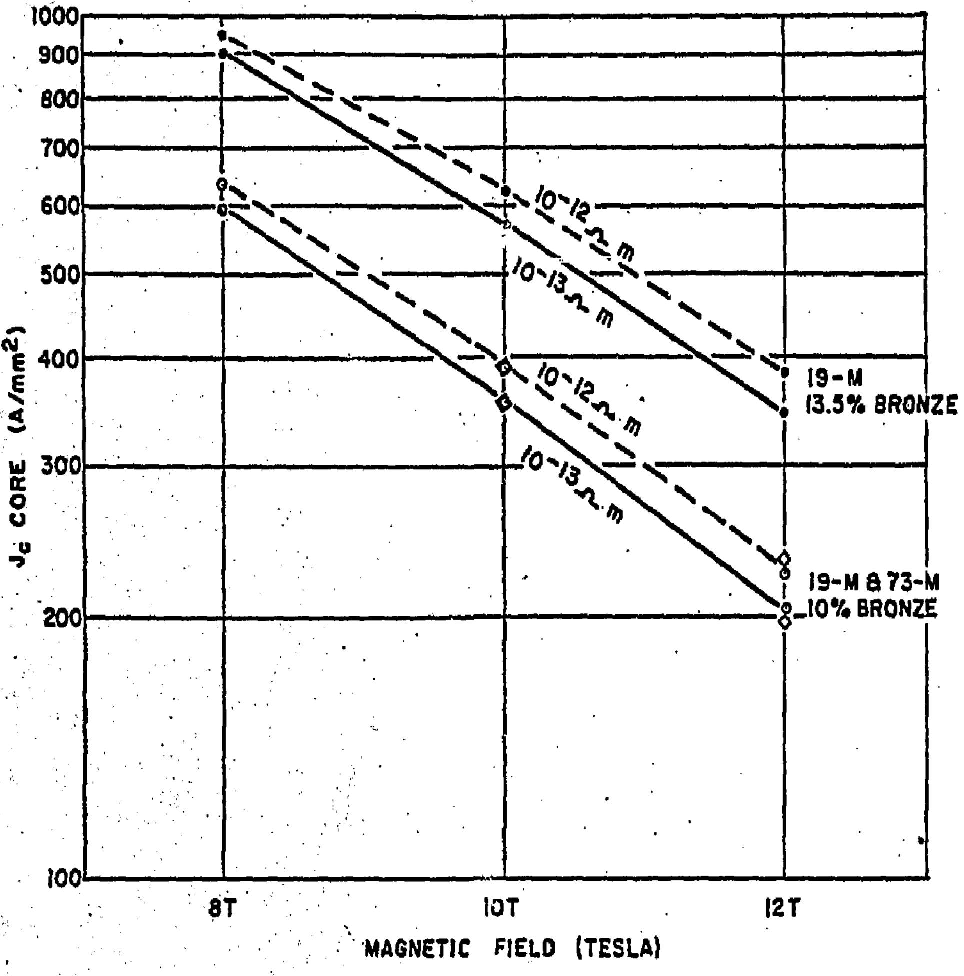


FIGURE 8.

CRITICAL CURRENT DENSITY IN (BRONZE + Nb + Nb_3Sn) CORES vs. MAGNETIC FIELD AT 4.2K FOR THIRD-STAGE CONDUCTORS.

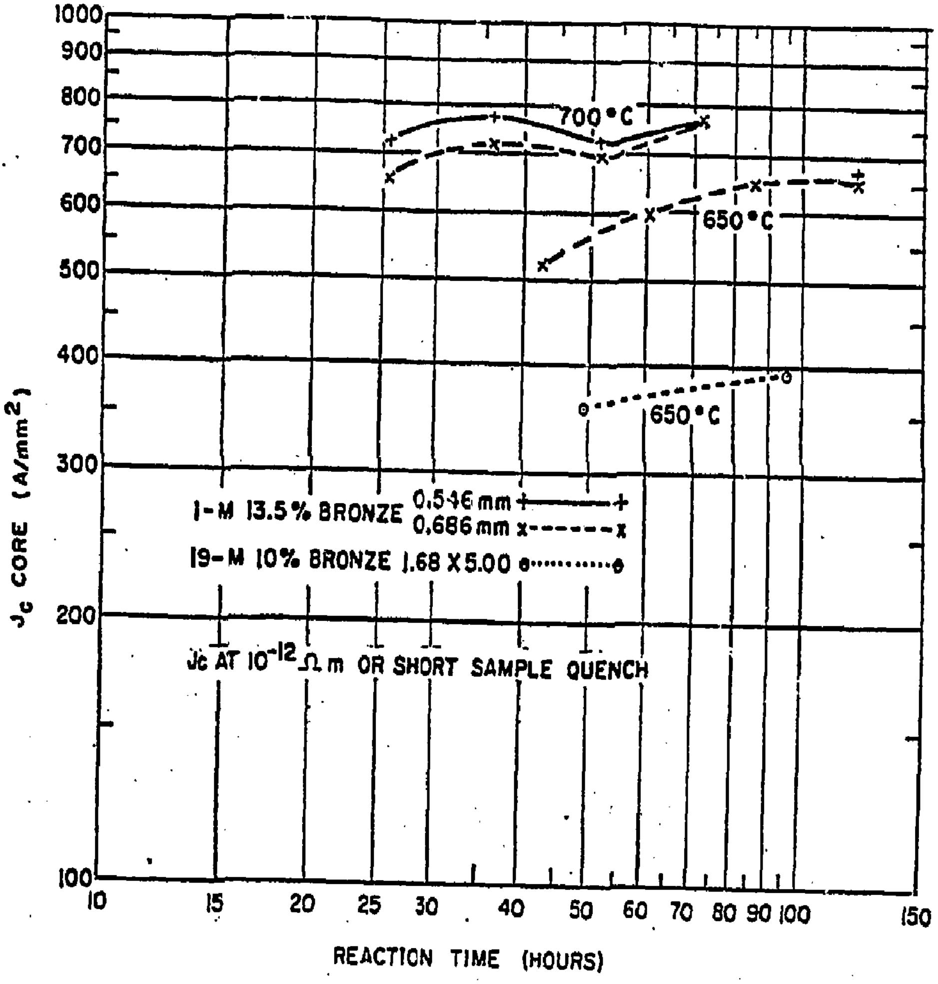


FIGURE 9.

CRITICAL CURRENT DENSITY IN (BRONZE + Nb + Nb_3Sn) CORES AT 4.2K AND 10T Vs REACTION TIME

TABLE I

MONOLITHIC STABILIZED MULTIFILAMENTARY Nb_3Sn SUPERCONDUCTORS

Bronze composition (wt. %)			10% Sn - 90% Cu		13.5% - 86.5% Cu		
Configuration			19-M	73-M	19-M	1-M	
No. of 19 Filament Hexes inside Ta liner inside Cu Shell in Second-Stage Module			187	187	283	283	
Final Stage Billet Dia. (mm)			50.7	101	75.7	110	
Total No. of Filaments			67,507	259 369	102 163	5377	
Composition before final reaction (Area %)	%Cu		34.0	34.0	34.0	10.8	
	%Ta		4.0	4.0	4.0	5.4	
	%Nb		12.9	12.9	15.9	21.5	
	%Bronze		49.1	49.1	46.1	62.3	
Conductor size (mm)			1.68x5.0	3.12x9.40	1.68x5.0	0.546 (dia.)	0.686 (dia)
Filament Diameter (µm)			4.5	4.3	4.1	3.5	4.3
Twist Pitch (mm)			50	100	40	10	6.4
at $10^{-12} \Omega$ m* or (QS) short sample quench	I_c (A) at	8T	3300		4950	151	238(QS)
		10T	2030	7200	3250		
		12T	1180	4300	2000		
	J_c core (A/mm^2) at	8T	634		950	770	768(QS)
		10T	390	396	624		
		12T	227	236	384		
at $10^{-13} \Omega$ m*	I_c (A) at	8T	3100		4675		
		10T	1860	6500	2975		
		12T	1060	3600	1800		
	J_c core (A/mm^2) at	8T	595		898		
		10T	357	357	571		
		12T	204	198	346		

* Resistivities are based on cross-sectional area excluding copper

I_c for 1-M conductor measured by Airco Central R & E Laboratories

TABLE II

ANALYSIS OF TANTALUM USED IN LINERS FOR 152mm DIA. SECOND-STAGE BILLETS (wt.%)

	Nominal Specification*	AIRCO Analysis
Nb	0.030 %	0.032 %
Si	0.001	0.011
Fe	0.001	<0.005
Ti	0.001	<0.005
W	0.007	0.027
Zr	0.005	<0.005
Mo	0.007	<0.005
C	0.0025	0.0017
H	0.0001	0.0001
N	0.0025	0.0035
O	0.010	0.0051

* Manufacturers Typical Analysis for "Select Quality Metallurgical Grade Tantalum"

< 0.005%. The lower limit of accuracy of our Atomic Absorbtion Analyzer is 0.005%