UCRL-13878

MASTER

FINAL REPORT

FOR THE

STUDY TO ASSESS THE FEASIBILITY OF SCALING UP

THE POWDER METALLURGY APPROACH FOR THE FABRICATION

OF COMMERCIAL Nb_3Sn FILAMENTARY SUPERCONDUCTORS

SUBMITTED TO:

LAWRENCE LIVERMORE LABORATORY

LIVERMORE, CALIFORNIA 94550

SUBMITTED IN ACCORDANCE WITH

LLL CONTRACT NO. 6903003

SUBMITTED BY:

MAGNETIC CORPORATION OF AMERICA

179 BEAR HILL ROAD

WALTHAM, MASSACHUSETTS 02154

DECEMBER 9, 1977

MCA WORK ORDER LLL-02

UNLIMITED

MAGNETIC CORPORATION OF AMERICA

I. INTRODUCTION

Under a contract from the University of California Lawrence Livermore Laboratory, Magnetic Corporation of America has undertaken a program to carry out a preliminary assessment of the feasibility of scaling up the laboratory techniques of making filamentary Nb_3Sn superconductors using powder metallurgy to commercial fabrication process. The purpose of the effort is divided into two tasks. The first one is to demonstrate that sintered niobium rods infiltrated with tin can be reduced in area of approximately 10^4. The second task pertains to the extrusion by conventional manner a copper billet containing several sintered rods each encapsulated in tantalum. The ultimate goal of the project is to establish optimal processing parameters that are suitable for the production of long lengths of fully stabilized, large current and high field conductors.

The report describes in detail all the efforts MCA has carried out in the next section titled Experiments and Results. The first part of the section deals with procurement of materials, finding vendor facilities for powder compaction, sintering and infiltration. The behavior of different grades of powders is also described. Under subheading of Task A, efforts to produce single core wire are reported. Task B details the work undertaken to conventionally extrude a 2" diameter billet. Based on the results of all the trials, tentative conclusions are drawn and are summarized in the last section.

II. EXPERIMENTS AND RESULTS

Two batches of niobium powder with particle size ranges of -200 +325 mesh and -100 +200 mesh were purchased from Teledyne Wah Chang Albany (TWCA). Two similar lots were also obtained from Kawecki Berylco Industries (KBI). The chemical analyses of the powder received from each source is shown in Table 1 and Table 2 respectively.

Initially, six rods measuring 0.6" diameter x 4.5" long were made by isostatically compacting the powder in Latex moulds at Thermoelectron Corporation, Waltham, Massachusetts. A hydrostatic pressure of 30,000 psi was employed. Four of the six rods were compacted from -100 +200 mesh TWCA powder, one from -200 +325 mesh TWCA powder and one from -200 +325 mesh KBI powder. The KBI powder was much harder to compact than the other. Pressures up to 40,000 psi did not result in rods with adequate green strength required for later handling. The powder with smaller particle size was slightly better than the larger size powder although both batches were from the same source. The higher oxygen and hydrogen contents in the KBI grades are believed to be primarily responsible for the powder hardness and thus poor compactability. However, an interesting feature of the KBI powder is that it yielded straighter rods than its counterpart.

Sintering operation was carried out at Centorr Associates in Suncook, New Hampshire. Modifications have been done on an existing shop furnace to facilitate both sintering and tin infiltration of single compacts in the same furnace system. An overall view of the furnace is shown in Figure 1. ([illegible]?) A total of 4 rods were sintered in a vacuum of about 5×10^{-5} mm of Hg for 15 minutes at 2260 to 2280°C. The infiltration was done by dipping each

TO ADDRESS Magnetic Corporation of America
179 Bear Hill Road
Waltham, Massachusetts 02154

TELEDYNE WAH CHANG ALBANY

P. O. BOX 460
ALBANY, OREGON 97321
(503) 926-4211 TWX (510) 595 0973

ATTENTION OF: Purchasing Department

IN REGARD TO YOUR PURCHASE ORDER NO 6127
ITEM NO 1 and 2
DESCRIPTION Columbium Powder
DIMENSIONS ---------
SPECIFICATIONS ---------

DATE 1-17-77
DATE SHIPPED Ref. P/L #1
QUANTITY SHIPPED As Listed
PRODUCTION ORDER NO 5380
XXXXXX Lot No. SR-2943

THE TEST REPORT FOLLOWS:

CHEMICAL ANALYSIS IN PPM

Al	<20	<20
C	<30	<30
Cr	<20	<20
Cu	<40	<40
Fe	<50	<50
H	6	10
Hf	<50	<50
N	25	33
Ni	<20	<20
O	390	550
Si	<50	<50
Ta	764	790
Ti	<40	<40
W	330	330
Zr	<100	<100

Item 1: 1 can, 5.1#
Item 2: 1 can, 4.9#

TABLE 1

RECEIVED
JAN 20 1977

ANALYSIS CERTIFIED BY ....
tn J. L. Forster, Ren.

KAWECKI BERYLCO INDUSTRIES, INC.

P.O. BOX 567

BOYERTOWN • PENNSYLVANIA 19512

TELEPHONE 215-367-2121 TELEX 836442

SOLD TO Magnetic Corp. of America
179 Bear Hill Road
Waltham, MA 02154

SHIP TO (IF OTHER THAN SOLD TO) Magnetic Corp. of America
179 Bear Hill Road
Waltham, MA 02154

ORDER NO.	DATE	SHIPPED VIA	CUST. P.O. # 6129
78122	1/27/77	UPS Zone 2 COD $569.18	BUYER K. Hemachalam

ITEM #	QUANTITY	UNIT	DESCRIPTION ☒ COLLECT ☐ PREPAID
			Correct P/L# 43747 Dated 1/10/77-Correct Description and Addition of Analysis
			Niobium Powder Metallurgical Grade
1	5	lbs.	Lot# WCB-300CD 200/325
2	5	lbs.	Lot#WCB-300CD 100/200
			Tantalum Tubing Annealed
1	1.36	lbs.	1 Pc. 2 Ft. Lot# 439 0.540" O.D. x .065" Wall x 24" Long

ANALYSIS

WCB-300CD

C	10 ppm	Cr	<10 ppm
O_2	825	Ca	<10
N_2	10	Na	<10
H_2	20	Al	<10
Ta	290	Mo	<10
Ti	<10	W	<10
Fe	50	Zr	<10
Mn	<10	Mg	<10
Si	<10	B	<10
Sn	<10	Co	<10
Ni	<10	Cu	10

Lot 439

C	15 ppm	Cr	<5 ppm
O	75	Ca	<5
N	10	Na	ND
H	<5	Al	<5
Nb	<25	Mo	<5
Ti	<5	Cu	<5
Fe	<5	Zr	<5
Mn	<5	Co	ND<5
Si	<5	Mg	<5
Sn	ND<5	B	<5
Ni	<5	W	ND<25

RECEIVED

JAN 31 1977

Complete

Attachment(s)

1. *Raw Materials*
   We certify that the raw materials used for the items listed conform to ~~your~~/commercial specifications.

2. *Product*
   We certify that the items listed conform to ~~your~~/commercial specifications and to your order.

3. Suitable evidence of compliance to your requirements is available in our files.

Specification No. ______

TABLE 2

Authorized Signature

SHIPPING NOTICE & CERTIFICATE OF COMPLIANCE Nº 4404

KAWECKI BERYLCO INDUSTRIES, INC.
P.O. BOX 567
BOYERTOWN • PENNSYLVANIA 19512

TELEPHONE 215-367-2181 TELEX 836442

SOLD TO: Magnetic Corp. of America
179 Bear Hill Road
Waltham, MA 02154

SHIP TO (If Other Than Sold To): Magnetic Corp. of America
179 Bear Hill Road
Waltham, MA 02154

ORDER NO.	DATE	SHIPPED VIA	CUST. P.O. # 6129
78122	1/27/77	UPS Zone 2 COD $569.18	BUYER K. Hemachalam

☒ COLLECT ☐ PREPAID

ITEM #	QUANTITY	UNIT	DESCRIPTION
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Fe	50	Zr	<10
Mn	<10	Mg	<10
Si	<10	B	<10
Sn	<10	Co	<10
Ni	<10	Cu	10

Lot 439

C	15 ppm	Cr	<5 ppm
O	75	Ca	<5
N	10	Na	ND
H	<5	Al	<5
Nb	<25	Mo	<5
Ti	<5	Cu	<5
Fe	<5	Zr	<5
Mn	<5	Co	ND<5
Si	<5	Mg	<5
Sn	ND<5	B	<5
Ni	<5	W	ND<25

RECEIVED
JAN 31 1977

Attachment(s)

Complete

1. *Raw Materials*
We certify that the raw materials used for the items listed conform to ~~your~~/commercial specifications.

2. *Product*
We certify that the items listed conform to ~~your~~/commercial specifications and to your order.

3. Suitable evidence of compliance to your requirements is available in our files.

Specification No. ______________

TABLE 2

Authorized Signature

SHIPPING NOTICE & CERTIFICATE OF COMPLIANCE

No. 4404

rod in a 700°C molten tin bath for about 2 minutes. To assure complete impregnation, the furnace was back-filled with gettered helium to a pressure of 2 psig. The first two sintering runs were made to get the Centorr Associates' personnel acquainted with the technique. As a result, those two rods were not considered to be suitable for further processing. Records of each run are kept on sheets, one of which is shown in Table 3.

Task A

Two more rods were sintered at 2260°C for 15 minutes and infiltrated with tin in exactly the same manner as above. Sections from top and bottom of each rod were prepared for metallographic examination. Small amounts of Nb_6Sn_5 were observed in the tin phase. The weight W and volume V of each rod are measured. The volume fraction of tin is calculated using the formula

$$\text{Volume Fraction of Tin} = \frac{V\,\gamma_{Nb} - W}{V\,(\gamma_{Nb} - \gamma_{Sn})}$$

where γ_{Nb} and γ_{Sn} are the specific gravities of niobium and tin respectively. Specific gravity values of 8.54 gm/cm^3 and 7.3 gm/cm^3 are taken for niobium and tin respectively. For the two rods, the calculated volume fractions of tin are 14% and 15%.

One rod was machined to 0.41" diameter, clad in 0.54" o.d. and 0.065" thick tantalum tube with a copper sleeve on the outside. The copper sleeve had a 0.92" x 0.92" square cross section with a 0.625" hole drilled in the center. The assembly was sent to Lawrence Berkeley Laboratory where it was cold-worked by roll-forming in square grooves. The final rolling pass resulted in approximately 0.25" diameter round cross section. The rods were then swaged to 0.222" diameter. Due to the severity of rolling, the outer copper had slit at some places along the length of the rod. Upon metallographic

NO. ____________________

Powder- Mesh: ____________________

Source: ____________________

Batch No.: ____________________

Compaction- Pressure: ____________________

Mould: ____________________

Rod Diameter: ____________________

Green Density: ____________________

Sintering-

Time:									
Temperature:									
Vacuum:									

Max. Power: ____________________

Temp. of Rods before dipping: ____________________

Infiltration- Temperature: ____________________

Time: ____________________

Backfilling: ____________________

Tin Vol. Fraction: ____________________

Cladding- Core Diameter: ____________________

Diffusion Barrier: ____________________

Outer Sheath: ____________________

Comments:

TABLE 3

examination, one crack extended to the [illegible] barrier. A micrograph of the center core is shown in Figure 2. The interconnected network of tin is seen as the dark phase. The rods were wire drawn at MCA at 15% reduction schedule. After the second die, the rods started to show evidence of internal breaking of the sintered core. Further drawing led to fractures with cup and cone configuration. When the rod diameter was 0.134", the copper was removed. Extensive internal factures 0.25" apart were observed within the tantalum clad which remained continuous.

The second infiltrated rod was slightly ground to 0.6" diameter and it was clad with 0.621" i.d. and 0.068" thick tantalum tube. The outer sheath was 0.826" i.d. and 1.054" o.d. copper tube. The assembly was swaged to approximately 0.9" diameter. The compact was further swaged in a four-jaw swaging machine at the University of Wisconsin, Madison. The die schedule that was followed is shown in Table 4. The final swaging pass was through 0.308" die. Sections were cut for metallographic study. A typical cross section is shown in Figure 3. As expected, the cross sections indicated a uniform reduction without any twisting of the core matrix unlike in the case of rods reduced by a two-jaw swager. When the rod was later subjected to wire drawing through a 0.289" die, it exhibited internal fracture at 3 places. More fractures appeared following the next pass through 0.267" die. As shown in Figure 4, the core seems to fail first with pores developing in the center. The easily flowing tin occupies the enlarging pores. As the pores become larger and larger, tensile instability sets in leading to fracture. The prime reason was considered to be a lack of ductility in the sintered cores.

FIGURE 2

TABLE IV

SWAGING DIE SCHEDULE

1)	0.840"	9)	0.475"
2)	0.750"	10)	0.450"
3)	0.710"	11)	0.425"
4)	0.675"	12)	0.392"
5)	0.640"	13)	0.362"
6)	0.600"	14)	0.340"
7)	0.570"	15)	0.334"
8)	0.540"	16)	0.308"

TABLE 4

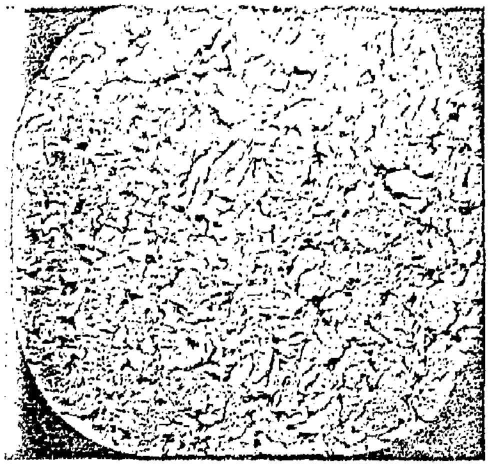

FIGURE 3

FIGURE 4

7.4.3

Further modifications to the Centorr furnace were made to facilitate sintering of 3 rods at a time. A new graphite tin bath was made to accommodate infiltration of the 3 rods. Two sintering runs were made to produce a total of 6 rods. To increase the tin content, the rods had been compacted at 25,000 psi. For 3 rods, the sintering duration is increased from 15 to 30 minutes in order to improve the ductility. Unfortunately, excessive outgasing from the furnace and the graphite tin crucible caused a poor vacuum in the low 10^{-4} torr range for the first run. For the second batch the vacuum was in the mid 10^{-5} torr range. The tin impregnation was done at 600°C to avoid any formation of intermetallics between niobium and tin. Top sections of all the rods and bottom sections of two rods were mounted for metallography. Typical micrograph is shown in Figure 5. Tin volume fractions varied between about 16% and 20%. The reason for this variation in the tin content is not known at this time.

A 2" diameter x 6.5" long, PDOF copper extrusion billet was designed as shown in Figure 6. Holes were drilled in the billet and reamed to 0.506" diameter. The infiltrated rods were machined to 0.461" diameter. The tantalum tube required to clad each rod is shown along with lids in Figure 7. The lids were machined out of Nb-45% Ti alloy rod. Prior to assembly, the rods, tubes and lids were acidicly cleaned. The rod assemblies were evacuated and electron-beam welded at both ends at Thermoelectron Corporation, Waltham. The copper billet and ~~one of~~ the welded rod composites are shown in Figure 8. Following insertion of cleaned elements, the extrusion can was evacuated and electron-beam welded to the lid.

The billet was extruded to 0.245" diameter rod at Nuclear Metals Inc.,

FIGURE 5

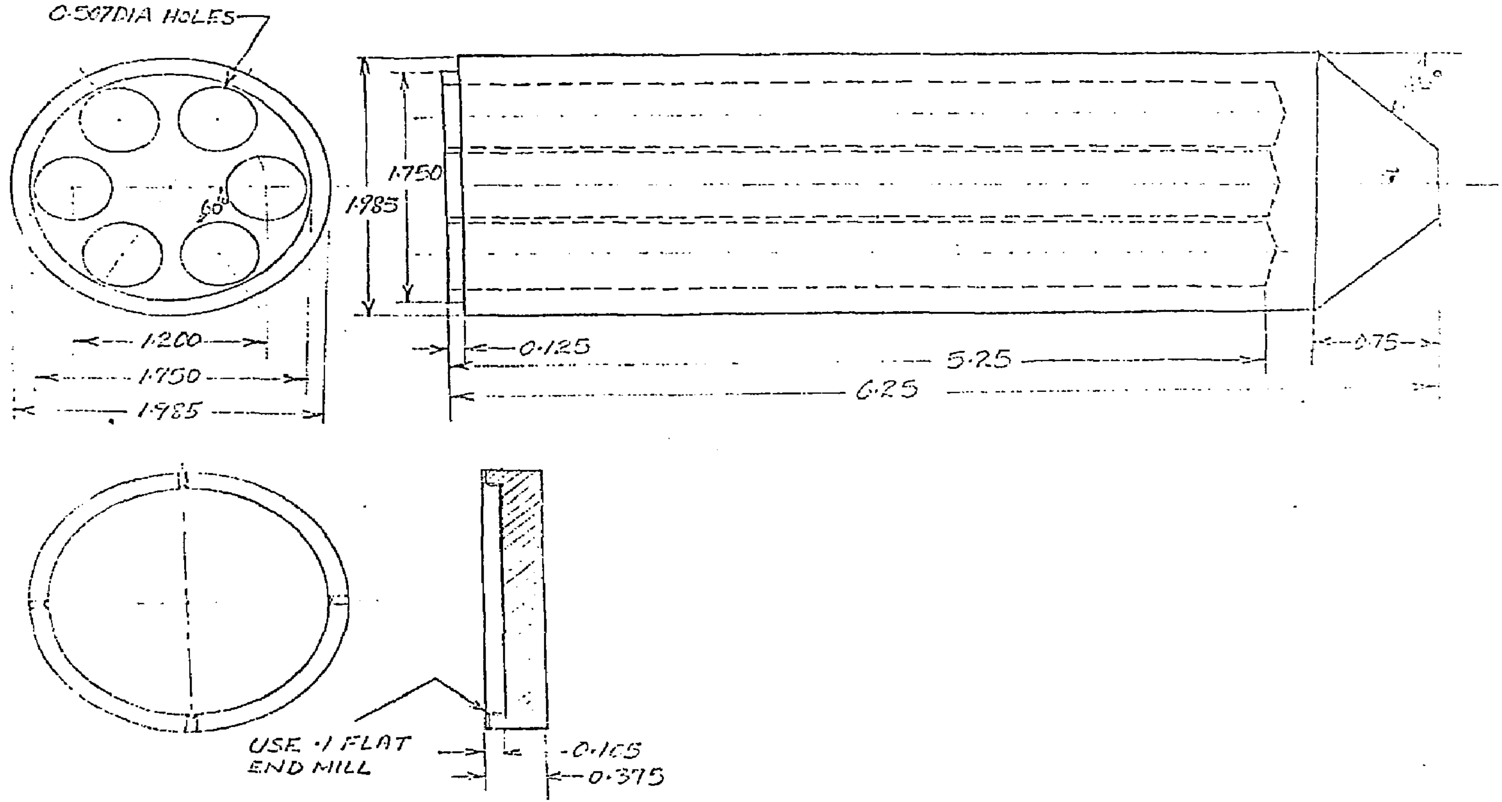
0.507DIA HOLES
60°
1.200
1.750
1.985
1.750
1.985
0.125
5.25
6.25
0.75
USE .1 FLAT
END MILL
0.165
0.375

FIGURE 6

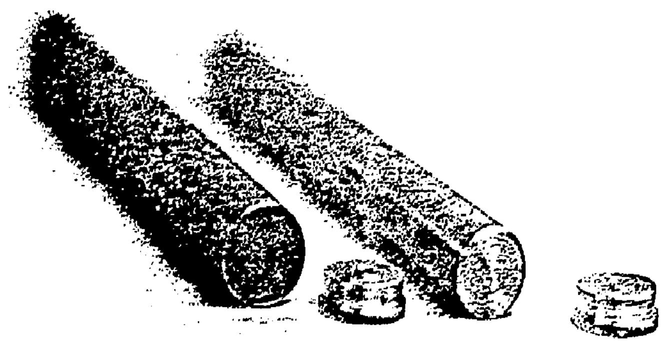

FIGURE 7

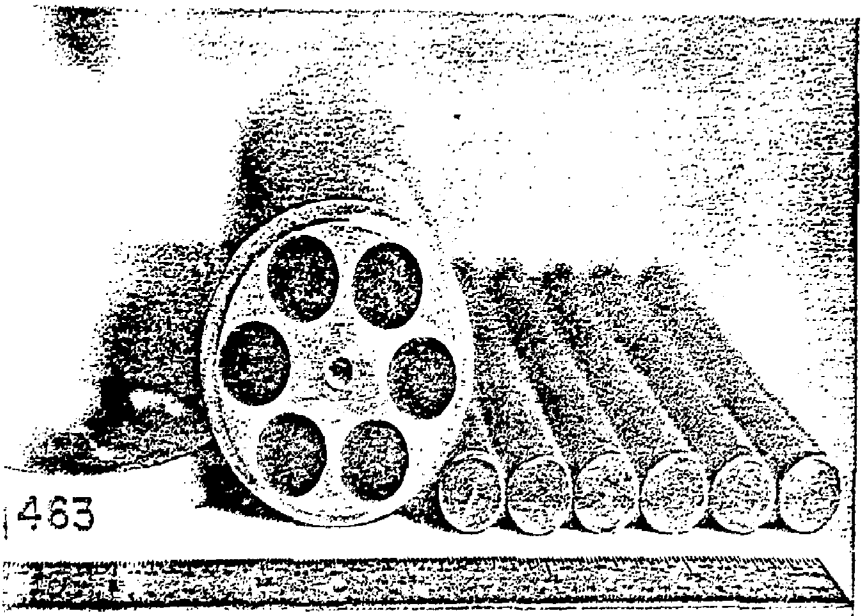

FIGURE 8

Concord, Massachusetts. Other extrusion details are as follows: liner and billet preheat ~ one hour to 415°C; upset load = 220 tons; running load = varied around 180 tons; extrusion speed = 25 ipm.

There was severe internal and external fracturing observed in the 105" long as extruded rod. Some tin had come out and got smeared on the surface. Visual examination indicated that the tin had escaped at several places including the transition points where the elements started and ended.

Three metallographic sections were cut 44", 47" and 105" from the leading end. Extensive element breaking was observed. It can be easily seen from the photomicrographs in Figures 9 and 10 that the sintered cores did not have enough ductility. It is believed that fractures in the cores led to the rupture of tantalum barrier sheath leading to direct contact of core material with the copper matrix. At the places of most severe damage the cracks had extended to the surface. Primarily, two types of surface cracks were observed. An arrowhead type extending only approximately one sixth of rod circumference might have been caused by internal fracture of one or two core elements at one point. The second type of cracks running perpendicular to the rod length were probably a result of two or more cores breaking inside.

There are several important features to be observed in the micrographs. One is the fact that in spite of the internal and external cracking, a considerable amount of tin had remained in the sintered cores. The other noteworthy feature is the non-mixing of tin into copper matrix where the tantalum sheath had ruptured. A microprobe examination at the interphase of copper and sintered core will be necessary to analyze the composition of various phases that may have formed during extrusion.

FIGURE 9

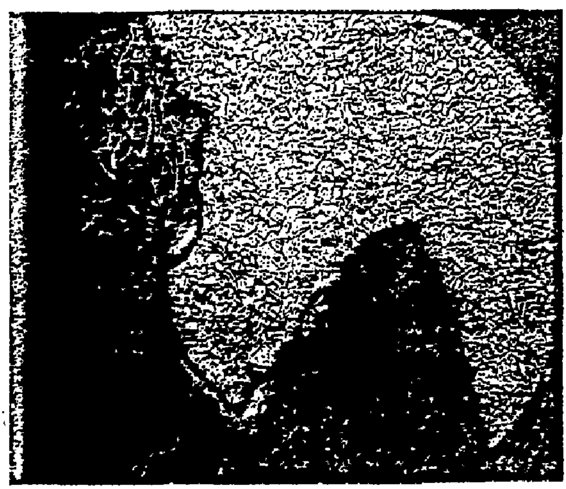

FIGURE 10

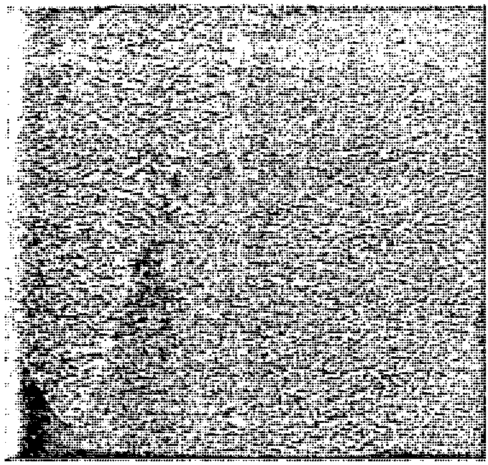

FIGURE 11

III. SUMMARY AND CONCLUSIONS

All efforts undertaken under both the tasks did not prove to be successful. The overriding cause appears to be the lack of ductility in the sintered and infiltrated cores. The area reductions achieved so far are far below those attained during previous research work at Lawrence Berkeley Laboratory. Starting at a 0.16" diameter, the cores were reduced to 0.006" diameter, i.e., a reduction ratio of 710. Unfortunately, the vacuum during sintering in the present work was poor. In spite of the failures, certain important observations can be viewed as encouraging. Coldworking single core composites in a four-jaw swaging machine resulted in a uniform reduction with no twisting of the niobium matrix. This type of swaging becomes useful to lengthen sintered cores before they are put in a multicore extrusion billet. Although tantalum barrier ruptured in many places in the 6-core extrusion, some tin remained in the niobium matrix. Furthermore, the tin did not contaminate copper where it came in contact with the latter. Therefore, it appears that when the ductility problem of the rods is solved, even with some tantalum rupture at the ends of the billet, the tin can be retained in the matrix.

Ductility is extremely dependent on the amount of interstitial impurities in niobium and on the roundness of the pores. These conditions are in turn functions of sintering temperature, time and vacuum. A quick and quantitative verification of the ductility is the microhardness of the niobium matrix. Microhardness measurements will be made on all metallographic specimens already cut from infiltrated rods. It is believed from discussions with the Berkeley group that a vacuum sintering in the 10^{-6} torr range at 2200 - 2300°C for one hour would be essential for achievement of enough ductility in the 0.5" diameter rods. The latest batch of rods sintered for 1 hour at 2290°C at mid 10^{-5} torr vacuum will be individually reduced to produce single core wires.