Conf 760505--1

LA-UR-76-360

**TITLE:** FABRICATION OF SUPERCONDUCTORS

MASTER

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**SUBMITTED TO:** ICED 6 Meeting, Grenoble, France, May 11-14, 1976.

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UNITED STATES
ENERGY RESEARCH AND
DEVELOPMENT ADMINISTRATION
CONTRACT W-7405-ENG. 36

# FABRICATION OF SUPERCONDUCTORS[*]

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## SUMMARY

The paper discusses the development of a process for making high performance, fine-filament superconducting wires, utilizing dual matrix stabilization and Nb46Ti superconducting filaments. Minimum filament size achieved was 8 μm using OFHC copper and Cu30Ni matrix materials. Ductility of the NbTi starting material was found to exert a major influence on the properties of the finished wire, and specifications for acceptable NbTi were developed. When specific impurity levels are exceeded, micron size precipitates and large inclusions are found. A rigorous stacking and extrusion procedure was developed. Very high density billets for extrusion were obtained by such techniques as co-drawing the stacking elements, contouring shells on a gear shaper and hydrostatic compaction. Extrusion parameters discussed are reduction ratios, temperatures, and working speeds.

## TEXT

### Introduction

For the past 30 months, a joint team consisting of Los Alamos Scientific Laboratory (LASL), Supercon, Intermagnetics General Corporation (IGC), Magnetic Corporation of America (MCA), and Teledyne Wah Chang Albany (TWCA), have been working on a process for NbTi (44 to 50 wt% Ti) superconducting

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[*] Work performed under the auspices of the U.S. Energy Research and Development Administration.

wire with fine filaments and a dual matrix of normal conducting materials for stabilization. The work entailed a reduction in filament sizes from 32 μm to ~ 8 to 16 μm.

The dual matrix of normal conducting materials consists of an oxygen-free, high conductivity (OFHC) copper sheath, surrounding each NbTi superconductor, embedded in a lattice of Cu30Ni.

Thirty months ago, the superconducting industry was producing multifilamentary wire with a single matrix of OFHC Cu and their problems consisted of an unreasonably high rejection rate and a limitation on filament size. Introduction of CuNi into the design forced a more rigorous extrusion process and an improvement in NbTi processing. Once these were accomplished, fine filaments were readily achieved and one can even argue that CuNi is an improvement in attaining finer filaments.

The basic manufacturing process was as follows:

- Make rods of NbTi.
- Assemble rods into copper tubing and stack both into an extrusion shell.
- Cap off the shell and extrude into bar.
- Bar draw.
- Wire draw.
- Heat treat the wire at ~ 4 times finish diameter, twist at ~ 1.2 times finish diameter, and anneal at finish diameter.

Influence of Copper Nickel Alloy

Incorporation of CuNi complicated the processing several ways:

- Of primary importance is the need to produce better filaments for equivalent electrical performance.
- CuNi requires a higher temperature than Cu to effect metallic bonding.
- CuNi creates higher internal heating than Cu during plastic deformation - a major concern during extrusion.
- CuNi conducts heat away to the tooling much slower than Cu.
- CuNi requires a higher annealing temperature than Cu.

## Extrusion Billet Assembly

The first operation improved was stacking superconductor elements into a container that could be extruded successfully. Billet sizes are limited by the cost benefits of using extrusion presses with capacities greater than 37 MN. Therefore, to obtain fine filaments, smaller diameter NbTi rod are stacked and increased billet density are needed. Co-drawing of NbTi rod, Cu tubing, and NiCu tubing was the first step. This eliminated two concentric clearance gaps occurring for each and every element.

Another source of "low density" is at the interface of the extrusion shell and the bundle of elements. Four processes to densify the starting billet were tried; two of which worked very well and one of which showed some promise.

The first method used was to make shells contoured on the i.d. to match the hexagonal stacking array as shown in Fig. 1. This was achieved by generating on a Fellows type gear shaper. A rack duplicating contour was cut, hardened, and ground. It was used to cut by generating a five sided "gear" cutter. The cutter then was used to regenerate the desired six sided contour. One minor complication arose: the cutter arbor deflected 0.102 mm during shaping. This problem was readily corrected by chemically milling the shell as required to obtain a free fit to the bundled elements. An estimated 99.5% as-assembled density was achieved using this procedure which eliminated associated problems during extrusion.

Shaping was performed from both ends by eliminating the integral nose and using a three piece assembly closed by electron beam welding. Use of a Cu nose, as compared to CuNi, reduced breakthrough forces by 40% - another major advantage.

The second method for densifying extrusion billets was equally successful and is probably preferable for designs incorporating more than 500 elements. Round rods of CuNi are assembled at the periphery, as in all methods of several years ago. However, the shell is now plastically deformed by hydrostatically pressing at 414 MPa at room temperature. This is sufficient to eliminate gaps at the periphery. There is, of course, no need to effect either metallic bonding or elimination of gaps between elements. Turning of the billet was required prior to extrusion in order to round its o.d.

A third method was used. It showed promise but was not adequate. Billets were assembled in the same manner as method No. 2, and were then compacted by hot isostatic pressing (HIPing) using argon. Adequate compaction was achieved at 922 K with 414 MPa in 7.2 ks. The temperature required was judged detrimental and so the process was discontinued. Any temperature above ~ 730 K probably degrades the NbTi rod. The later success with room temperature hydrostatic pressing demonstrates how easily "HIPing" could be improved.

The fourth method investigated was rotary swaging. It proved unsatisfactory because the shell elongated during plastic deformation and some working of the outer elements occurred.

Extruding

Extrusion practices at the onset of this effort were only fair. The die reduction ratio of 16:1 was proper. Ram speeds were 12 to 25 mm/s and far too high - adiabatic heating was occurring. Preheating temperatures of 890 to 1005 K were too high. Over-temperature had the following deleterious effects:

- Resulted in Cu diffusion into the NbTi.
- Resulted in Ti diffusion into the Cu.
- Maximized the formation of precipitates in the NbTi.

The entire effort was therefore to reduce the temperatures as much as possible while still obtaining metallic bonding during extrusion. This was achieved in the following manner:

- Preheating was performed at 780 K for copper matrix and 905 K for dual matrix.
- Ram speeds were reduced to 3.4 mm/s for both Cu and dual matrix.
- Only very pure CuNi alloys were used, with Cu30Ni around each element and Cu10Ni for the shell.
- Die reduction ratio of 10:1 was used for dual matrix extrusion.
- Water quenching immediately subsequent to extrusion was made an essential, not occasional, practice.

For the future, it would probably be worth investigating the effect of extruding at temperatures of ~ 700 K on wire performance. This requirement would probably necessitate using hydrostatic film extrusion.

## Drawing

Bar drawing and wire drawing were routinely employed with no problems. No efforts were made to optimize the schedule. Once standard NbTi rod is obtained such work would probably be worthwhile.

## Heat Treating

Very few modifications were made in the procedure as a result of the subject effort. The effects of the process were analyzed with the following fascinating thoughts:

- The major heat treat removes the dislocation tangles but does not affect grain and subgrain structure.
- The best grain structure is achieved by a process whereby the NbTi is reduced in area at least $2 \times 10^3$:1 during the drawing stage.
- No indications of secondary phases such as α-Ti, ω or martensites were noted.

## Niobium-Titanium Processing

The major discovery of the entire program has been that more ductile NbTi makes better wire. A proposed guideline is that the NbTi is processed so as to yield a ductility of > 90% RA in a tensile test. To achieve this, the following conditions must be met:

- The rod must be fully recrystallized with a fine grain structure of ASTM No. 6 or greater.
- The rod must be helium gas quenched to 420 K from 1075 K in 5 min or less.
- Hydrogen levels must be less than 20 ppm.*
- Nitrogen levels must be less than 80 ppm (assuming existing oxygen levels of ~ 800 ppm).
- Carbon levels must be less than 80 ppm.
- Insoluble metallic impurities must be below the following:

| | |
|---|---|
| Copper | 40 ppm |
| Sn | 40 ppm |
| Al | 50 ppm |

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* ppm by weight.

Wire with a measured critical current density, $J_c$, of $2.8 \times 10^5$ A/cm$^2$ at 30 kg and 4.2 K was obtained by adhering to these specifications. The photomicrograph shown in Fig. 2 was obtained for a dual matrix wire.

When the criteria were not met the degree of degradation corresponded to the deviation. Figure 3 shows rod with an acceptable, although not desirable, precipitate. The precipitate in itself is fascinating. There is electron microprobe and ion mass microprobe evidence to indicate these to be a mixture of complex oxides of niobium and titanium which involve most of the metallic impurities, e.g., $LiAlTiO_4$, $FeTiO_3$, $FeNb_2O_6$, etc.

Should the impurities become even greater, a very large (up to 50 μm) inclusion results. Figure 4 shows such an inclusion in optical metallography, Fig. 5 shows a similar one by SEM. To date, all such inclusions appear to be of a composition similar to the precipitate.

The inclusions rapidly lead to filament necking, and fracture, during the wire drawing stage. Figure 6 shows a typical wire. Generalized precipitation also leads to filament necking as shown in Fig. 7. We have noted that wire performance roughly approximates the necking condition for dual matrix wire. Copper matrix wire is far more tolerant of necking, a convincing argument for current jumping between adjoining filaments. We believe that it would be possible to adjust somewhat for precipitates by modifying the drawing schedule and having less reduction per pass.

## FIGURES

Figure 1. Hexagonal stacking array for extrusion billet.

Figure 2. Cross-section of a typical dual matrix wire of 0.419 mm diameter.

Figure 3. Recrystallized, gas quenched Nb-46Ti, 660X.

Figure 4. Impurity inclusion in the surface of a metallographically prepared specimen of Nb-48Ti, 1000X.

Figure 5. Impurity inclusion exposed on the fracture surface of Nb-46Ti, 3000X.

Figure 6. Cross-section of a typical wire with filaments necked due to inclusions, 250X.

Figure 7. NbTi filaments necked due causes other than inclusions, 170X.

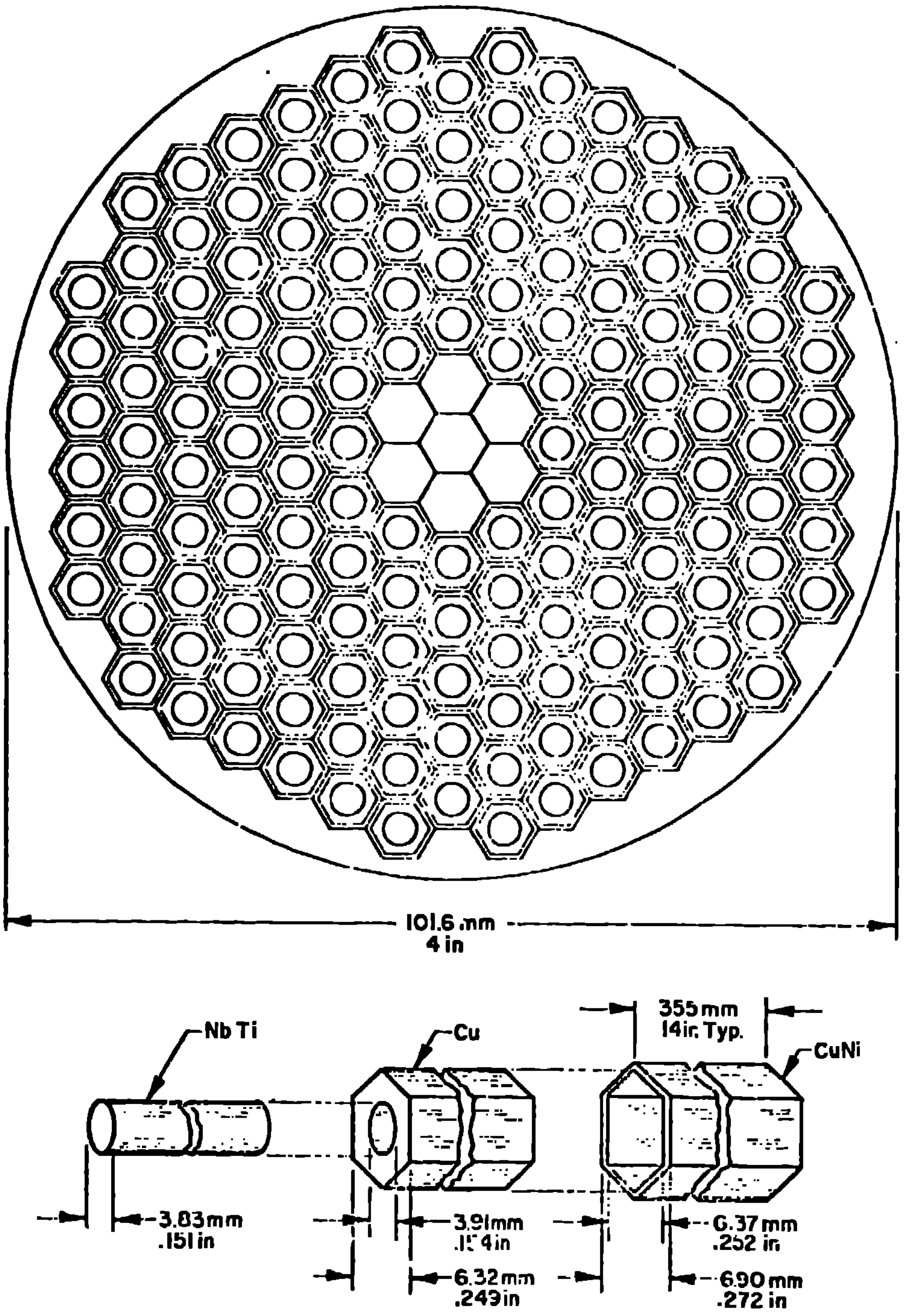
101.6 mm
4 in
Nb Ti
Cu
355 mm
14 in Typ.
CuNi
3.83 mm
.151 in
3.91 mm
.154 in
6.32 mm
.249 in
6.37 mm
.252 in
6.90 mm
.272 in

Fig. 2

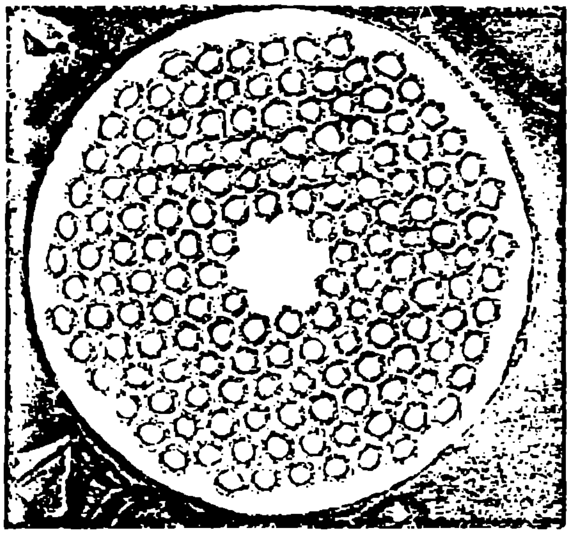

Fig. 3

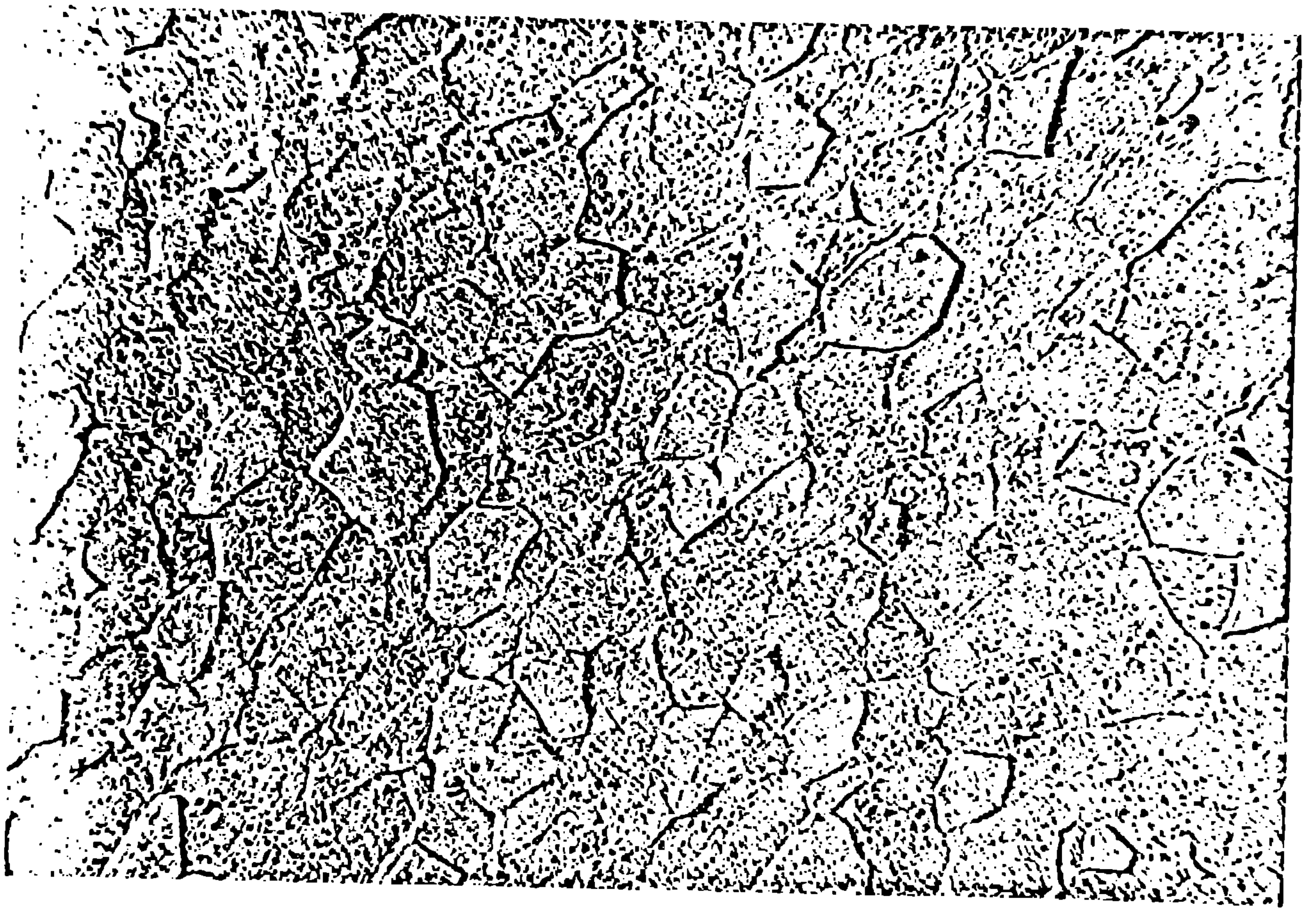

Fig. 4

Fig. 5

Fig. 6

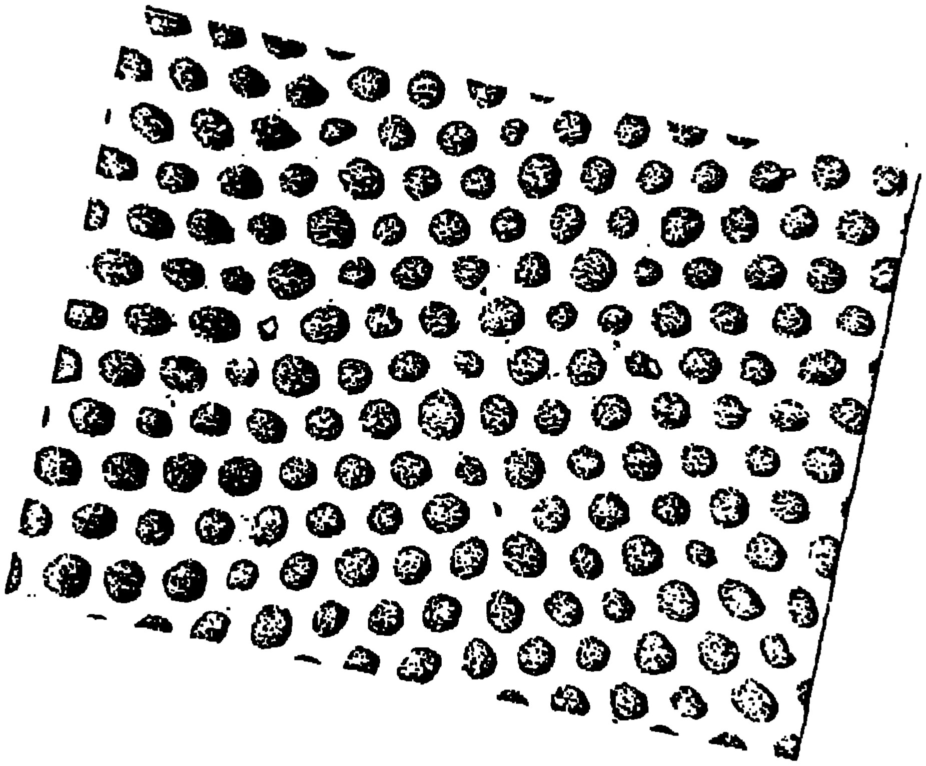

Fig. 1