

[54] **STABILIZED SUPERCONDUCTORS**  
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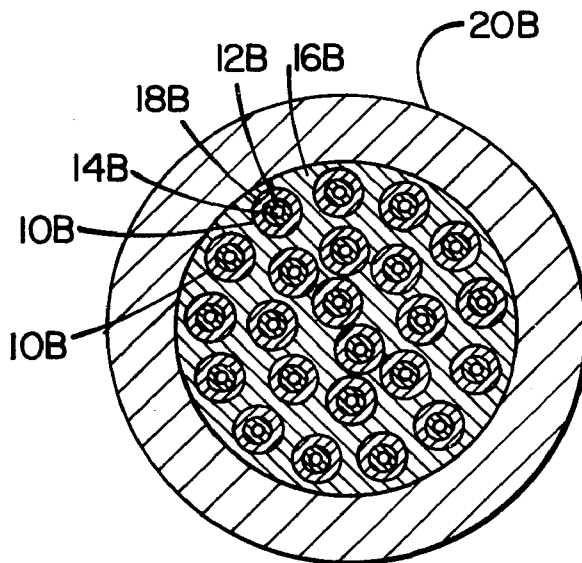
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[52] U.S. Cl. .... **148/32; 29/599; 148/34;**  
174/126 CP  
[51] Int. Cl.<sup>2</sup> ..... **H01L 39/00; H01B 12/00**  
[58] Field of Search ..... 148/34, 32, 11.5 R;  
29/599, 191.6; 174/126 CP, DIG. 6

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[57] **ABSTRACT**  
A stable, high field, high current composite wire comprises multiple filaments in a depleted bronze matrix, each filament comprising a type II superconducting, Beta-Wolfram structure, intermetallic compound layer jacketing and metallurgically bonded to a stabilizing copper core, directly or via an intermediate layer of refractory metal.

**6 Claims, 3 Drawing Figures**



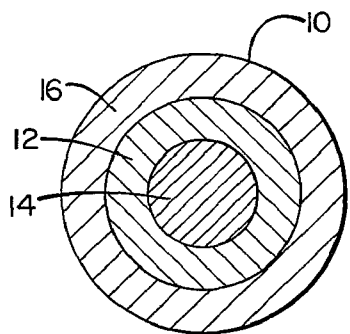


FIG. 1

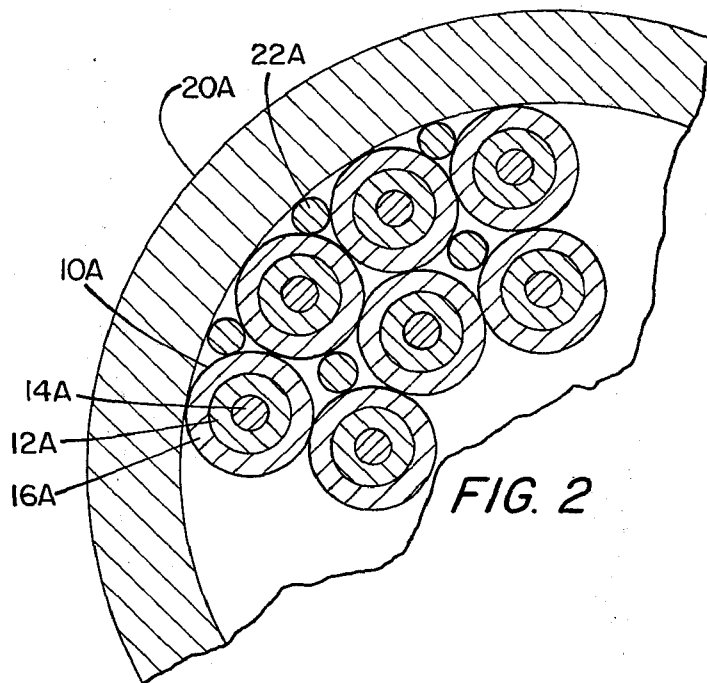


FIG. 2

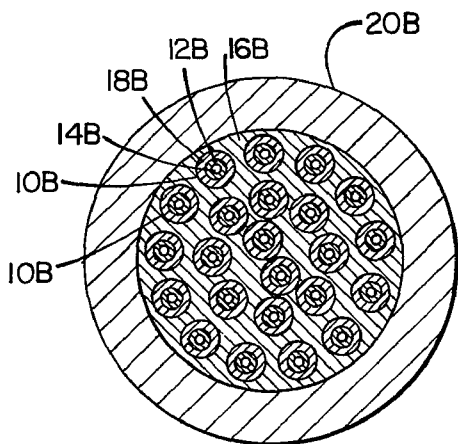


FIG. 3

## STABILIZED SUPERCONDUCTORS

## BACKGROUND OF THE INVENTION

The present invention relates to superconductors and more particularly to Type II superconductors made of intermetallic compounds of Beta-Wolfram structure.

Work in the U.K. (see U.S. Pat. No. 3,728,165 to Howlett and U.S. Pat. No. 3,472,944 to Morton et al. and U.S. Pat. No. 3,807,041 to McDougall), in the U.S. (see U.S. Pat. No. 3,731,374 to Suenaga et al. and U.S. Pat. No. 3,838,503 to Suenaga et al.) and in Japan (see Applied Physics Letters January, 1974, Furuto et al.) has involved the production of Type II superconductors by reaction of spaced niobium or vanadium filaments in a wire with gallium or tin supplied from a bronze matrix of the wire. While materials of the above type show considerable promise for high field superconductors, they are somewhat limited in their stability. They fail to utilize all their intrinsic critical current capacity due to instability. The art has utilized wires comprising spaced filaments niobium-titanium alloy in pure copper matrix to a substantial degree despite the lower intrinsic critical currents of such alloys at high magnetic fields, compared to Beta-Wolfram compound superconductors.

It is an important object of the invention to provide Beta-Wolfram compound based wire and wire braid or cable products which have sufficient stability to enable realization of a greater portion of their intrinsic current carrying capacity.

It is a further object of the invention to provide such Beta-Wolfram compound based products which are sufficiently ductile to be used in electromagnetic coil winding and like wire or wire braid and cable fabrication and usage.

It is a further object of the invention to make available the practical utilization of the high field, high current characteristics of the Beta-Wolfram compounds together with the electrical stability and mechanical characteristics of alloy conductors for magnetic coils, rotating electrical machinery, power transmission and the like.

As used herein, "wire" includes wires and wire-like ribbons, flattened wires and the like. Resistance ratio means ratio of electrical resistance measured at room temperature (300°K) to resistance measured at liquid helium temperature (4.2°K). "Metallurgical bond" means metal to metal bonding between layers essentially free of nonmetallic phases.

## SUMMARY OF THE INVENTION

In the present invention, a multifilamentary product is provided wherein the filaments comprise annular layers of niobium (for example) which are converted in part to Nb<sub>3</sub>Sn and each filament comprises a core of high conductivity copper having a resistance ratio greater than 100 which imparts stability to the composite superconductor. This is achieved, in a preferred form of the invention when niobium and tin are used to form the niobium stannide superconductor, by providing a niobium tube which is filled with a pure copper core, this tube being inserted, along with a number of similar tubes, into a billet made by drilling spaced longitudinal holes in a tin-bronze ingot. Alternatively, many such tubes may be jacketed with bronze and packed together in a sheath to form a composite billet.

The composite billet is then reduced by suitable mechanical treatments such as extrusion, swaging, rolling,

drawing and the like until the wall thickness of the niobium tubes has been reduced to about 2-5 microns. Thereafter, the product is heated to a temperature on the order of 750°C for 0.5 to two hours to react most of the tin within the bronze matrix with part or almost all of the niobium tube but preferably leaving at least a 2-4 micron niobium layer to provide strengthening reinforcement and protection of the copper core from contamination by diffusing tin.

The tin is not entirely consumed. Enough tin remains in the bronze matrix so that the bronze has the high resistance (at 4.2°K, or to put it another way, low resistance ratio) characteristics of an alloy or impure copper rather than the high resistance ratio of pure copper. However, the pure copper core in each filament retains its high resistance ratio characteristic throughout processing. The high resistance residual bronze matrix provides stabilization under conditions of pulse current operation.

The same processing may be applied to formation of superconductors using other refractory metals, e.g. vanadium, molybdenum, and other bronze matrixes, e.g. gallium-bronze, to form other superconductive compounds of Beta-Wolfram structure.

The unreacted portion of the refractory metal layer of each filament is metallurgically bonded to the superconductive compound layer, formed at refractory layer/bronze matrix interface, and is also metallurgically bonded to the copper core essentially throughout the filament length and, since the filaments are continuous throughout the composite wire length, such metallurgical bonding is continuous throughout the wire length. The superconductive compound layers of the filaments are, in essence, then metallurgically bonded to their respective pure copper cores. This provides the wire with enhanced stability compared to the above described composites and does so consistent with high current, high field specifications.

The residual (unreacted) portion of the refractory metal layer provides a strengthening reinforcement which is put under compression under conditions of cooling to cryogenic temperatures to induce superconductivity of the compound layer compressive stress is also induced in the Nb<sub>3</sub>Sn layer.

It is a further feature of the invention that in case of breach of the niobium tube walls of random filaments during working, tin contamination is limited to the copper cores of such filaments only and does not affect other filaments.

The end product conductor combines the high field, high critical temperature benefits of Beta-Wolfram compounds with the stability of the alloy conductors. The conductor of the invention may be used in production of magnets for plasma research at fields above 10 Tesla, large alternating current generators, inductive energy storage, particle accelerator and bubble chamber magnets, NMR apparatus, and homopolar motors, and as power line conductors and in other devices utilizing one or more of the benefits of higher field, higher current or higher temperature operation compared to state of the art devices of the same kind.

The above and other objects, features and advantages are now described in the following detailed description of preferred embodiments, taken in connection with the accompanying drawing in which:

## BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a cross-section view of a multi-layer component rod for packing in a matrix according to a preferred embodiment of the invention;

FIG. 2 is a cross-section view of a packed matrix incorporating several of the FIG. 1 rods; and

FIG. 3 is a cross-section view of the composite wire product produced from the FIG. 2 packed matrix.

## DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

Referring now to the drawings and more particularly FIG. 1 thereof, there is shown a cross-section of an assembled component used in practicing the process of the invention. The component 10 comprises a seamless tube or centrally bored rod of refractory metal 12 encasing a core 14 of pure copper. The refractory metal is selected from the group consisting of niobium and vanadium and their fabricable alloys including niobium-015 to 5.0 weight percent (w/o) zirconium; niobium-1 to 30 w/o tantalum; niobium-1 to 10 w/o molybdenum; vanadium-chromium, vanadium-titanium. Ternary or quaternary alloys may also be utilized in lieu of the elemental or binary alloy forms of vanadium and niobium. Niobium-1 w/o Zr is preferred high strength refractory metal.

The component further comprises an outer tube 16 of a tin bronze. The bronze may be modified by addition of such elements as germanium, aluminum, or silicon as will produce a beneficial type II ternary compound upon subsequent diffusion heat treatment. The tin bronze may be used with niobium or niobium alloy jackets and the gallium bronze may be used with vanadium or vanadium alloy jackets.

The component is preferably prepared by pre-assembly in large sizes such as 0.5 to 12 inches outer diameter and 0.43 to 11.5 inches outer diameter and 0.35 to 9.0 inches diameter for core 14 with no spacing therebetween as may be accomplished by sinking or shrink fit techniques well known in the art. The thus assembled billet may be extruded or swaged to produce a long rod of 1/16 to 3/4 inches outer diameter (all layers having proportional reduction on an areal basis corresponding to the areal billet to rod reduction ratio). The rod is cut to lengths of 6 to 24 inches.

Referring now to FIG. 2, a multiplicity of rod lengths 10A, formed as described above in connection with FIG. 1, are packed into a copper alloy tubular form extrusion billet 20A, selected for its fabricability compatibility with the refractory metal. Additional wires 22A of pure copper or bronze can be included in the interstices of the pack. The outer diameter of tubular billet 20A would be 2 to 12 inches and the inner diameter would be 90 to 95% thereof.

The components 10A comprise layers 14A, 12A, 16A corresponding to original layers 14, 12, 16 respectively. From 6 to 30,000 of the rod lengths 10A are packed into billet 20A. The billet has a nosed front end and is capped at its back end in accordance with conventional extrusion practice. It is extruded through an area reduction ratio of 10 to 100 times at a temperature of 500° to 650°C, extrusion force of 180 to 12,000 tons and speed of 10 to 40 inches per minute; quenched; and further worked by swaging and drawing. In the course of swaging or drawing, intermediate heat treatments of 500° to 650°C for 0.5 to 1 hour may be made

on the composite product to counteract work hardening. Such anneals are preferably made after each 50% area reduction.

After the product reaches final wire size, the wire product is twisted at a rate of 0.1 to 15 twists per inch of running length and then subjected to a final heat treatment of 700° to 750°C for 1/2 to 100 hours for diffusion reaction of the niobium with tin from the bronze matrix.

The resultant composite wire product, shown in FIG. 3, typically of about 10 mils diameter comprises a spaced array of filaments 10B in a bronze matrix 16B enclosed by outer copper alloy layer 20B. Each filament comprises a superconductive compound outer layer 18B having a radial thickness of zero to two microns and having typically 8-10 micron outer diameter and a residual refractory metal layer 12B having a 4-5 micron inner diameter and encasing a copper core 14B.

The wire drawing may be stopped at larger sizes than 10 mils, e.g. as high as 1/4 inch square or 1/4 inch diameter, and resultant filament and filament component layer sizes will be correspondingly larger compared to those of the 10 mil diameter wire product described above.

The wire may be made with complete or partial consumption of the niobium or other refractory metal layer of each filament. Partial consumption is preferred to provide the residual refractory metal layer as a contamination barrier and strengthening reinforcement. Even if the structural integrity of refractory metal layers is breached in random filaments, tin contamination is limited to local areas because the copper cores of other filaments are protected by their respective Nb<sub>3</sub>Sn/Nb jackets.

It is evident that those skilled in the art, once given the benefit of the foregoing disclosure, may now make numerous other uses and modifications of, and departures from the specific embodiments described herein without departing from the inventive concepts. Consequently, the invention is to be construed as embracing each and every novel feature and novel combination of features present in, or possessed by, the apparatus and techniques herein disclosed and limited solely by the scope and spirit of the appended claims.

What is claimed is:

1. Superconductive multi-filament wire product comprising,

means defining a bronze matrix with a plurality of spaced filaments therein,

each of the filaments comprising a layer of type II superconducting intermetallic compound of Beta-Wolfram structure being the diffusion reaction product of a first elemental component derived from said bronze matrix and of a second elemental component derived from source filaments comprising a refractory metal outer layer,

means defining within each filament a copper core having a resistance ratio greater than 100 and being essentially free of said elemental components, and

the compound layers of the filaments being metallurgically bonded to the copper core.

2. Superconductive multi-filament wire product in accordance with claim 1 wherein said compound comprises Nb<sub>3</sub>Sn, said refractory metal comprises niobium and said bronze comprises tin.

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3. Superconductive multi-filament wire product in accordance with claim 2 and further comprising, a residual niobium layer in each filament metallurgically bonded to the compound layer thereof, said niobium layer being metallurgically bonded to said copper core.

4. Superconductive multi-filament wire product in accordance with claim 1 and further comprising, a residual refractory metal outer layer in each filament underlying the compound layer thereof, said refractory metal layer being metallurgically bonded to said compound layer and to said copper

core.

5. Superconductive multi-filament wire product in accordance with claim 1 wherein said compound comprises  $V_3Ga$ , said refractory metal comprises vanadium and said bronze comprises gallium.

6. Superconductive multi-filament wire product in accordance with claim 5 and further comprising, a residual vanadium layer in each filament metallurgically bonded to the compound layer thereof, said vanadium layer being metallurgically bonded to said copper core.

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