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METHOD OF MAKING DUCTILE SUPERCONDUCTORS

Filed Aug. 12, 1963

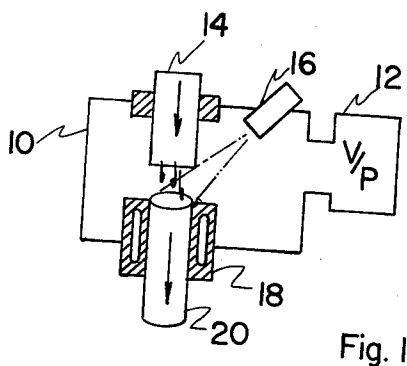


Fig. 1



Fig. 2

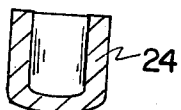


Fig. 3

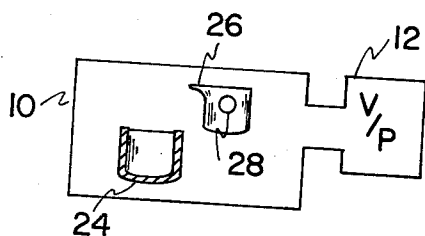


Fig. 4

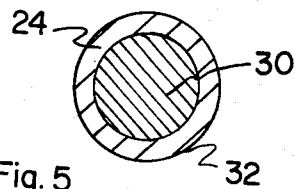


Fig. 5

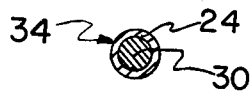


Fig. 6

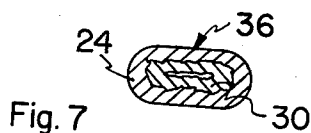


Fig. 7

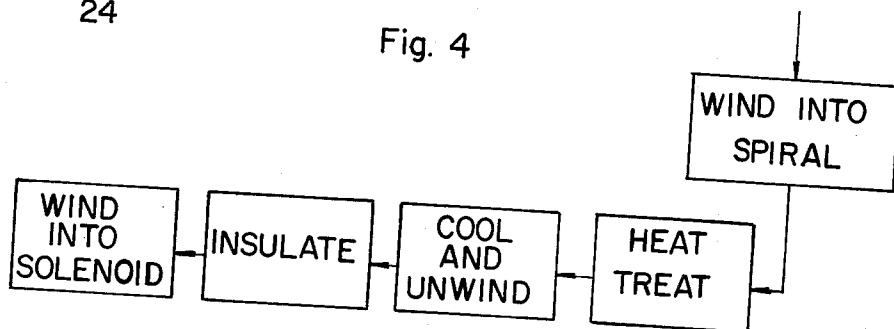


Fig. 8

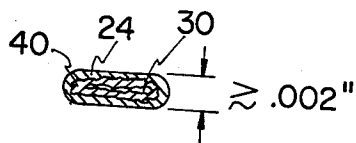


Fig. 9

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METHOD OF MAKING DUCTILE SUPERCONDUCTORS

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This application is a continuation in part of my copending applications S.N. 208,925 filed July 10, 1962 and S.N. 233,961 filed Oct. 29, 1962.

The present invention relates to elongated superconductors of ribbon form used in winding magnetic coils and the like. Specifically, the present invention relates to metallic ribbon having a diffusion layer of a hard superconductor intermetallic alloy of sufficiently small thickness that the ribbon is bendable. Such diffusion layers are described in my above copending applications.

The present invention provides another specific embodiment of the method of interdiffusing the components of a hard superconductor alloy to form a thin diffusion layer of the alloy which is bendable.

It is a principal object of the invention to provide a method of making a hard superconductor in ductile form which will be characterized by freedom from contamination, improved diffusion and improved performance.

It is another object of the invention to provide a method of making a hard superconductor which permits a simple heat treatment.

The invention is applicable to hard superconductor alloys comprising, as a higher melting point component, one or more of niobium, tantalum and vanadium, and, as a lower melting point component, one or more of tin, gallium, thallium, silicon, aluminum, germanium, and indium.

In a preferred embodiment of the invention, a superconductive ribbon comprising a sheath of niobium surrounding an inner diffusion layer of Nb_3Sn is produced. The ribbon will be capable of being wound about a $\frac{3}{8}$ " diameter mandrel without breaking a majority of the internal superconducting paths.

For a fuller understanding of the nature and objects of the invention, reference should be had to the following detailed description in conjunction with the accompanying drawings, wherein:

FIG. 1 is a schematic view of the first step of the process of the invention;

FIG. 2 is a cross-section of the product of the invention at an early stage of treatment;

FIG. 3 is a cross-section of the product at a later stage of treatment;

FIG. 4 is a schematic view of a still further treatment;

FIG. 5 is a cross section of the product after the treatment indicated in FIG. 4, the section being typical of any cross-section along the length of the product except for the ends thereof;

FIGS. 6 and 7 are typical cross-sections of the product after further treatments;

FIG. 8 is a block diagram of final treatments; and

FIG. 9 shows the resultant product in cross-section. According to the present invention, the new method is carried out in the following sequence of steps:

- (1) Electron beam melting of niobium.
- (2) Pressing into a disk.

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- (3) Spinning the disk into a tube (several passes with vacuum annealing after each pass).
- (4) Vacuum casting tin into the tube.
- (5) Furnace cooling.
- (6) Rolling and drawing the tube down to wire.
- (7) Flattening the wire to ribbon.
- (8) Winding the ribbon into a spiral.
- (9) Heat treatment.

Conventional metallurgical processes are utilized in all the steps. Steps 1 and 4 and the anneals of Step 3 are carried out in a vacuum furnace. The temperature of the niobium tube and molten tin in Step 4 should be maintained at about 300° C., after initially annealing the niobium at higher temperature, with the vacuum furnace pressure below 10⁻⁵ torr. The cooling of Step 5 may also be accomplished by removing the tube from the hot furnace and cooling in air.

The attack of atmospheric contaminants is limited by quick freezing of the tin in air. At this point, the tube comprises a sheath of niobium and a core of tin with little formation of Nb_3Sn and other contaminants at the interface between the core and sheath.

Then the tube is cold drawn down to wire utilizing the method of Allen, Das and Stauffer, disclosed in the copending United States applications, S.N. 193,281 filed May 8, 1962 and S.N. 278,723, filed May 7, 1963. This method involves the use of substantial cold work reduction to extend the interface between the niobium and tin to insure high purity by dispersing contaminants over the extended interface. This insures ease of wetting of the niobium by molten tin upon subsequent heating in Step 9. After a reduction in area of the sheath and core in excess of about 30:1, the resultant wire is flattened by passing through cylindrical rolls to form ribbon. The ribbon is wound into a tight spiral. The spiraled ribbon is then heated in the vacuum furnace for an hour at about 1100° C. to form a diffusion layer of Nb_3Sn at the interface between the niobium and tin. After completion of the heating step, the spiral can be unwound since the tin is trapped inside the niobium ribbon and cannot leak out to cause adjacent turns to stick. The resultant ribbon is ductile and can be rewound into solenoids and the like without destroying its superconductive properties.

Referring now to the drawings, the steps of the process are now described with respect to a preferred embodiment using Nb_3Sn as an example of the superconductor to be formed.

Niobium is purified by electron beam melting as shown in FIG. 1. The melting is carried out in a vacuum chamber 10 evacuated below 0.1 micron by vacuum pump 12. A niobium bar 14 or powder stock is fed into the path of an electron beam produced by an electron gun 16. The beam melts niobium which is collected and degassed in a cold mold 18 and finally withdrawn as a high purity ingot 20.

The ingot 20 is pressed into the form of a disk as shown in FIG. 2. The disk is spun into the form of a tube 24, shown in FIG. 3, having a $\frac{1}{2}$ inch outer diameter and .040 inch wall thickness. The tube 24 is thus of high purity and free of seams or other joints.

The niobium tube 24 is returned to the vacuum chamber 10 where it is annealed under a vacuum of 10⁻⁵ mm. Hg. at a temperature between 1000° C. and 1400° C. for one hour. The chamber is provided with a crucible 26 and crucible pivots 28. Tin is melted in the crucible at 300° C. and under a vacuum of 10⁻⁵ mm. Hg. Then

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the crucible is tilted to vacuum cast the tin into tube 24. Tube 24 is cooled and then removed from the furnace. The resultant product is a cylinder 32 comprising a niobium sheath 24 and a solid tin core 30, as shown in FIG. 5. Cylinder 32 is capped by crimping the open end. Then cylinder 32 is rolled and drawn down to wire size to form the wire 34 of FIG. 6. The rolling and drawing is carried out in accord with the teachings of Allen, Das and Stauffer in their U.S. patent application, S.N. 193,281, filed May 8, 1962. The diameter of the resultant wire 34 is on the order of .010 to .020 inch after a reduction of cross-section area in excess of 30:1. The extensive reduction creates new surface at the niobium-tin interface, thus dispersing the residual contaminants therein to improve the cleanliness of the interface.

Wire 34 is flattened between pressure rolls to form the ribbon 36 of FIG. 7. Ribbon 36 is then drawn to form a reduced thickness ribbon which is less than about .002 inch thick. The ribbon comprises an unbroken, seamless sheath of niobium surrounding a flattened core of tin.

The ribbon is then fabricated into a solenoid according to the steps outlined in FIG. 8. The heating is carried out between 900° C. and 1200° C. for ½ to two hours. The clean niobium surface is readily wettable by molten tin and the reaction proceeds rapidly and uniformly. At the end of the heating cycle, the ribbon is removed from the furnace and cooled in air. The ribbon may then be insulated by a conventional plastic whereas the insulation of prior art core wires would be a special high temperature ceramic insulation because the prior art cores must be insulated before heat treatment.

FIG. 9 shows the ribbon at the end of the heat treatment step. The sheath 24 then comprises a diffusion layer 40 of Nb₃Sn at the inner surface of the sheath. The core 30 comprises residual tin and small void spaces. Essentially, no niobium or Nb₃Sn particles are found in the core, apart from the niobium and Nb₃Sn trapped in the sheath's inner diffusion layer.

The present invention is particularly applicable to vanadium gallium which can only be formed with great difficulty in prior art core wires and is a very brittle compound. In applying the technique of the present invention, the tube 24 of FIG. 4 (which would be vanadium) should be capped by inserting a stopper in the open end of the tube after pouring the gallium and indenting the tube into depressions in the stopper. This will hold the low melting gallium during the drawing process. The process of the present invention guards the highly reactive gallium from contamination.

A principal advantage of the present invention is that the ribbon is heat treated before insulating and forming into a coil. It is not necessary to apply an expensive ceramic insulation as in prior art core wires. A cheap plastic insulation can be used. A related advantage is that the reactive tin or gallium or indium, etc. is trapped inside the ribbon. The ribbon can be wound into a compact spiral, inserted into a furnace muffle, and then heat treated and readily unwound after heat treatment. A ribbon with the low melting component on an outer surface would pose problems of adjacent turns sticking if wound into a tight spiral and heated.

The above-described preferred embodiment has several advantages over the prior art. The flattened form of the final product permits a higher ratio of length of Nb₃Sn diffusion layer to total cross-section area than a round wire because the geometry of a ribbon is inherently more favorable and because ribbons can be cold worked to smaller thicknesses more readily than wires. The ribbon form inhibits the formation of voids during the heat treatment and is a more favorable shape than round wire for winding coils. The wire 34, comprising a soft core 30 of tin and no hard materials, is readily flattened.

The process permits the use of high purity sheath material and vacuum degassed core material. The clean core material is degassed while held in crucible 26 and while being transferred from vacuum degassing crucible 26 to tube 24. The tin is then trapped in the tube without exposure to oxidizing agents and other contaminants which would limit the effectiveness of the subsequent heat treatment.

Other advantages are afforded by maintaining a continuous sheath of pure niobium about the core throughout the cold work and heating steps. The leakage of tin is prevented and the niobium-tin interface is protected from contaminants.

In comparison to the known core wires of the prior art, the present invention offers the further advantage of confining the superconductive alloy to a thin diffusion layer which permits bending of the finished product and entails shorter times of heat treatment compared to the 20 hour heat treatments needed for prior art core wires.

Since certain changes can be made in the above product and process without departing from the scope of the invention herein involved, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

What is claimed is:

1. A method of making ductile superconductors providing high current densities through an internal layer of an intermetallic alloy hard superconductor comprising the steps of placing a tube made of a higher melting component of the alloy in a non-oxidizing atmosphere and annealing it, maintaining the lower melting point component of the alloy in a non-oxidizing atmosphere in molten state to degas it, pouring the molten metal into the tube while maintaining their temperatures below the reaction temperature at which their brittle intermetallic alloys are formed, cooling the tube, cold working the tube down to wire size to extend the interface between the core and sheath thereby making the sheath readily wettable by the core materials, cold rolling the wire to flatten it to ribbon form and to further reduce its cross section thickness after flattening the wire to ribbon form, and then heating the ribbon at the reaction temperature to form the desired intermetallic, hard superconductor alloy as a diffusion layer inside the ribbon.

2. A method of making ductile superconductors providing high current densities through an internal layer of an intermetallic alloy hard superconductor comprising the steps of placing a tube made of a higher melting component of the alloy in a non-oxidizing atmosphere, maintaining the lower melting component of the alloy in said atmosphere, in molten state, pouring the molten metal into the tube while maintaining the temperatures of the tube and molten metal below the reaction temperature at which their brittle intermetallic alloys are formed, cooling the tube, then drawing the filled tube down to wire size, to extend the interface between the core and sheath thereby making the sheath readily wettable by the core materials, then flattening the tube to ribbon, and then heating the ribbon at the reaction temperature to form the desired intermetallic alloy as diffusion layer at the inner surface of the sheath.

3. The method of claim 2 wherein the higher melting component is niobium and the lower melting component is selected from the class consisting of tin, gallium, thallium, silicon, aluminum, germanium, indium, and mixtures thereof.

4. The method of claim 3 wherein the higher melting component is niobium and the lower melting component is tin and the reaction temperature is maintained between 900 and 1200° C.

5. The method of claim 4 wherein the ribbon is cold rolled to reduce its cross section thickness to less than .002 inch before heat treating at the reaction temperature.

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6. The method of claim 2 wherein the higher melting component is selected from the class consisting of niobium, tantalum and vanadium, and mixtures thereof.

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