

[54] **METHOD OF MANUFACTURING A DUCTILE SUPERCONDUCTIVE MATERIAL**

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[51] Int. Cl. **H01v 11/00, B22f 3/24**

[58] Field of Search **29/599, 420, 420.5, 182.1, 29/192 R, 194, 197, 198, 183.5, 191, 191.2, 191.4, 191.6; 174/126 CP, DIG. 6**

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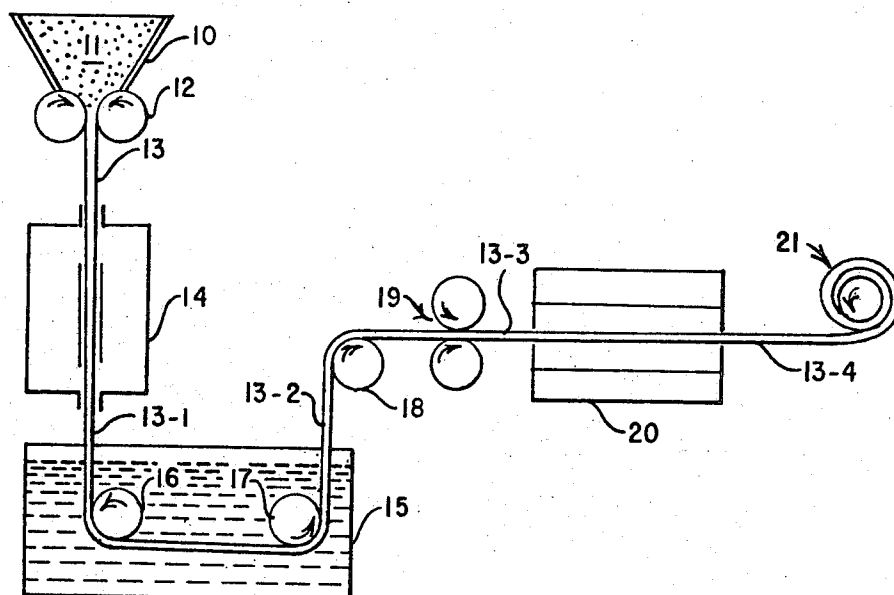
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[57] **ABSTRACT**

A ductile superconductive material and method for manufacturing same, which basically may utilize any porous metal or its hydride with a melting point substantially higher than that of the infiltrating metal that will form a superconductive compound when reacted with the infiltrating metal. The superconductive material is made from a porous strip or tape of niobium or vanadium for example, infiltrated with tin, aluminum, antimony, antimony, or gallium, for example, and treated in a manner so as to contain interconnecting filaments of the superconducting phase Nb₃Sn, Nb₃Al, Nb₃(Al,Ge), Nb₃Sb, or V₃Ga, for example. The novel manufacturing process, which is relatively simple and inexpensive provides a method of producing a new and useful end product capable of a broad superconductive range due to the amount of reaction of the infiltrated material with the porous material. The novel process may be utilized in either batch or continuous operational applications.

13 Claims, 4 Drawing Figures



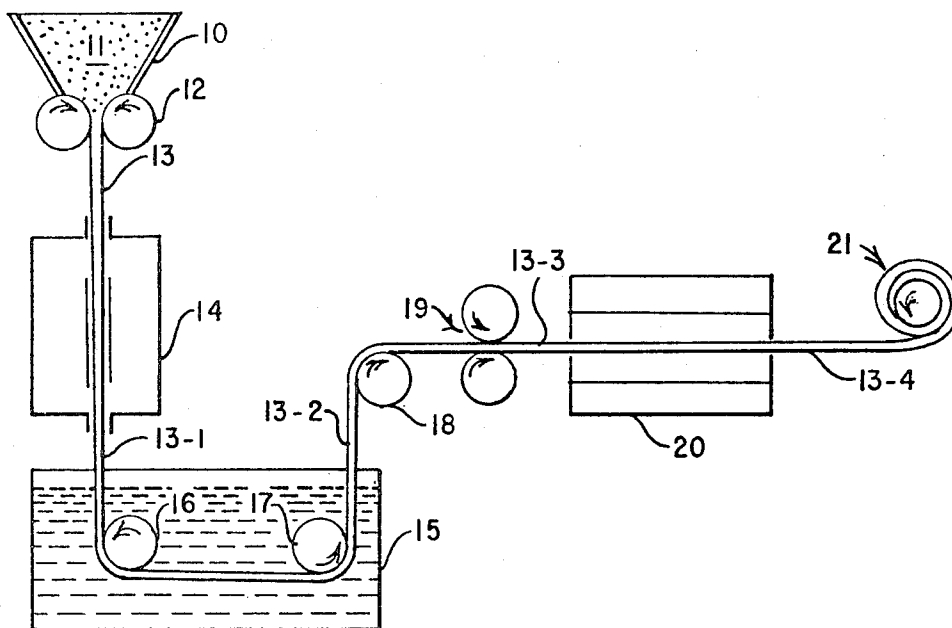


FIG-1

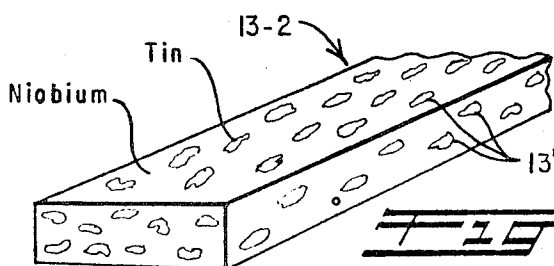


FIG-2

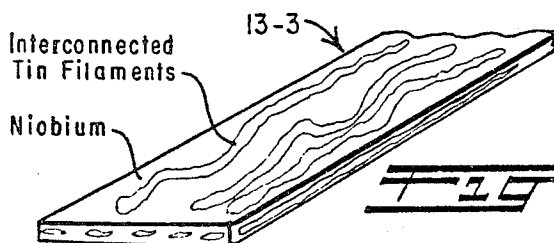


FIG-3

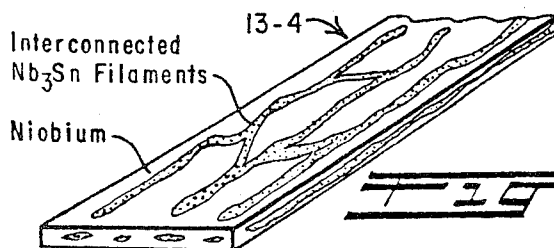


FIG-4

METHOD OF MANUFACTURING A DUCTILE SUPERCONDUCTIVE MATERIAL

BACKGROUND OF THE INVENTION

The invention described herein was made in the course of, or under Contract No. W-7405-ENG-48, with the United States Atomic Energy Commission.

This invention relates to superconductive material, and more particularly to an improved superconductive material and method of manufacturing.

When cooled to extremely low temperature, certain metals and alloys lose their resistance to the passage of an electric current and are then called superconductors. Once a flow of current has been started in a superconductor, it will continue in a closed circuit indefinitely, even after the source of the current is removed.

An electromagnet with the exciting current carried by coils of a superconducting material would function with little or no power expenditure except that required to maintain the necessary low temperature. The problem in the construction of such superconducting magnets of appreciable size has been the difficulty of producing wire with satisfactory physical and mechanical properties at a reasonable cost. In recent years, certain metallic compounds (alloys) of niobium, e.g., with tin, titanium, or zirconium, have been developed for fabrication into superconducting wires. While the prior art efforts have resulted in substantially improving the state of the art of superconductive materials, the prior processes have been complicated and expensive, thus illustrating a need in this field for an effective superconductive material that can be manufactured by a relatively simple and inexpensive process.

SUMMARY OF THE INVENTION:

The present invention provides a ductile and effective superconductive material that can be produced relatively simply and inexpensively by either batch or continuous production. Basically the invention involves the forming of a porous strip or tape from niobium or vanadium powder, for example, sintering the strip, infiltrating tin, aluminum, germanium, antimony, or gallium, for example, into the pores of the niobium or vanadium strip, and diffusion heating treating the infiltrated strip forming interconnecting filaments of the superconducting phase Nb_3Sn , Nb_3Al , $Nb_3(Al,Ge)$, Nb_3Sb or V_3Ga , for example, throughout the strip. The amount of the superconducting phase is varied by controlling the time and temperature of the heat treatment. Also, the novel process may include reduction of the infiltrated strip, such as by rolling, prior to the diffusion heat treatment which has a significant effect on the conversion of the infiltrate to the superconducting phase during the subsequent heat treatment thereof. Hydrides of the metals, e.g., niobium hydride can be used in place of the element. The hydrides decompose to form the porous metal during the sintering process.

Therefore, it is an object of the invention to provide a superconductive material and method for manufacturing same.

A further object of the invention is to provide a ductile superconducting material containing interconnected filaments of a superconducting phase throughout the material.

Another object of the invention is to provide a process for manufacturing a superconductive material containing interconnected filaments of Nb_3Sn , Nb_3Al , $Nb_3(Al,Ge)$, Nb_3Sb or V_3Ga .

Another object of the invention is to provide a method of manufacturing a superconducting material which includes forming a strip of porous niobium from niobium powder, infiltrating the porous strip with tin, aluminum, aluminum-germanium, or antimony, and selectively treating the infiltrated niobium strip to form interconnecting filaments of the superconducting phase Nb_3Sn , $Nb_3(Al,Ge)$, or Nb_3Sb throughout the strip.

Other objects of the invention will become readily apparent from the following description and accompanying drawing.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a schematic illustration of an apparatus for carrying out the operational sequence in a continuous method for making superconductive material in accordance with the invention; and

FIGS. 2-4, illustrate typical structures of the niobium-tin (Nb_3Sn) embodiment of the inventive superconductive material in various stages of processing in accordance with the invention.

DESCRIPTION OF THE INVENTION

While the following description is directed primarily to the niobium-tin (Nb_3Sn) embodiment for purposes of illustration, it is not intended that the greater detailed description of this embodiment limit the invention to this specific embodiment in that, as pointed out above and as set forth in greater detail hereinbelow, that the invention can be carried out with other superconductive compound such as niobium-aluminum-germanium, $Nb_3(Al,Ge)$; niobium-aluminum, Nb_3Al ; niobium-antimony, Nb_3Sb ; and vanadium-gallium, V_3Ga . While efforts conducted thus far to verify the invention have been directed to the above-mentioned compounds, it is currently believed that the porous base metal of the strip may be any porous metal with a melting point substantially higher than that of the infiltrating metal that will form a superconductive compound when reacted with the infiltrating metal.

Referring now to FIG. 1 wherein an embodiment of an apparatus is illustrated schematically for carrying out the operational sequence for manufacturing the niobium-tin (Nb_3Sn) embodiment of the superconducting material as partially illustrated in FIGS. 2-4. While the illustrated process is of the continuous type, it may be modified for batch type production if desired.

A hopper 10 containing finely powdered niobium 11, for example, of particle sizes ranging from -100 mesh to -400 mesh, is mounted above a compacting roller mechanism indicated at 12 which, when rotated in the direction indicated by the arrows, produces a "green" strip or tape 13 of porous niobium, the interconnected pores being indicated after filling with tin at 13' in FIG. 2. For example, with the compacting roller mechanism 12 having 2 inch diameter rolls and a roll gap of 0.012 inch, a "green" strip 13 having a thickness of ≈ 0.015 inch is produced. The "green" strip 13 is passed through a sintering furnace 14 having, for example, either vacuum or an inert gas atmosphere, a temperature in the range of 1,950-2,250°C, for a time of about 3 minutes, for example, for a thin strip. The sintered strip

indicated at 13-1 coming out of the furnace 14 has interconnected pores and a porosity which can be controlled over a considerable range. By way of specific example: Density = 6.71 GMS/cm³ = 78.3 percent of theoretical density $\cong$ 21.7 percent porosity. Sintered strip 13-1 is passed through a molten tin bath 15 having direction changing rollers 16 and 17 around which the strip 13 passes, where the porous niobium is infiltrated (pores filled) with tin producing a tin infiltrated strip indicated at 13-2 (see FIG. 2), the tin filled pores being indicated by legend. For example, the molten tin bath temperature is in the 500°–1,000°C range, and the immersion time of the strip 13-1 in bath 15 is in the range of a few seconds to several minutes. As tin infiltrated strip 13-2 emerges from bath 15 it passes over a direction changing roller 18 and through a thickness reduction rolling mechanism generally indicated at 19 wherein a cold reduction of the tin infiltrated strip indicated at 13-3 is accomplished due to the strip being ductile (see FIG. 3), the interconnected tin filaments shown by legend in FIG. 3. Reductions in thickness of the order of 75 percent, for example, presents no problem. However the cold reduction operation is optional depending on the desired thickness of the strip and the heat treating of the strip as described hereinafter. The thus rolled tin infiltrated strip 13-3 is then passed through a diffusion heat treating furnace 20 wherein the tin is converted to Nb₃Sn (See FIG. 4), and the converted strip now indicated at 13-4 is rolled or reeled on a take-up spool apparatus 21 or other suitable collecting mechanism. The diffusion temperature of the strip in the furnace 20 may be up to about 1,100°C with a preferred range of 925°C to 1,075°C, with a time at that temperature being from less than 1 minute to several hours. As pointed out above, the desired superconducting phase is Nb₃Sn. By controlling the amount of prior deformation, the time and temperature of heat treatment, part or all of the infiltrated tin may be converted to Nb₃Sn.

If desired, the diffusion heat treatment of the tin infiltrated strip 13-3 may be accomplished by passing the strip through a bath or molten tin instead of furnace 20.

Also, if desired the diffusion heat treating operation can be carried out as a separate process. The infiltrated strip 13-3 can be coiled directly on the reel 21, and subsequently heated in an inert atmosphere or vacuum to produce the superconductive phase as above described. This would be a desirable modification of the above described process for materials that must be heated for long periods of time at low temperatures to produce the superconductive phase. An example of this is V₃Al.

By way of example, with no prior cold reduction of the tin-infiltrated niobium strip, a heat treatment of 2 hours at 975°C (ductility: nil) results in appreciable amounts of unreacted tin; while with a prior reduction in thickness of 75 percent, a heat treatment for only 1 minute at 1,000°C (ductility: can be formed around a $\frac{3}{8}$ inch diameter mandrel) results in conversion of a major portion of tin to Nb₃Sn.

To illustrate the advantages of the inventive superconductive material, current density tests have been conducted to determine the current carrying capacity of specific strips of the material. However, it should be noted that the current density will vary with different materials and process variables such as the porosity of

the strip (which determines the maximum amount of infiltrate that can be infiltrated into the strip), the amount of reduction of the infiltrated strip, and the heat diffusion time and temperature which determine the amount of reaction between the porous strip and the infiltrate, and thus determines the critical current required to drive the material from a superconductive state to a normal state. By way of example only, niobium powder of -270 mesh was rolled into a strip, sintered, infiltrated with tin, reduced about 75 percent forming a strip having a cross-section of 0.004 inch by 0.055 inch, and diffusion heat treated in accordance with the invention. The thus formed strip of Nb₃Sn was wound on a mandrel and tested for critical current density by placing the coil in a variable magnetic field and varying the amount of current passed through the coil. The tests were conducted in magnetic field settings of 15KG, 20KG, and 50KG. To determine the amount of current flow through the coil required to drive the coil normal voltage readings across the coil were taken. A detectable voltage reading indicated the start of the transition to the normal state. For example, with the coil as above described, the tests showed the starting of the transition to normal as being 8.7×10^4 , 7.0×10^4 and 3.1×10^4 amps. per sq. cm. for the 15, 20 and 50KG magnetic fields respectively. The cross-section utilized to determine the above amps/sq. cm. values is the cross section of the ribbon or strip. In this specific test the volume fraction of Nb₃Sn in the strip was estimated to be about 7 percent. Accordingly, it is readily apparent that by increasing the volume fraction of the Nb₃Sn by the processing variables indicated above, the current carrying capacity of the strip would be substantially increased.

After the completion of the above current density test the strip was reverse wound on the mandrel, and retested with the result that there was no substantial reduction in the current carrying capacity. This clearly verifies the ductility of the inventive superconductive material.

As pointed out above, the inventive superconductive material is not limited to the niobium-tin (Nb₃Sn) embodiment set forth above, other embodiments manufacturable by the inventive process will be briefly described hereinafter to more fully illustrate the novel concept.

For the binary niobium-aluminum (Nb₃Al) embodiment, the molten bath 15 contains aluminum at about 800°C with good infiltration of the aluminum into the niobium strip being obtained in less than 1 minute, the remainder of the process being the same as above described.

In the ternary niobium-aluminum-germanium—Nb₃(Al,Ge) — embodiment, an aluminum-germanium eutectic (approximately 53 percent by weight of germanium) having a melting point of 424°C was used as the infiltrate in the molten bath 15, with the molten eutectic being maintained at a temperature of about 700°C, and with an immersion time of the niobium strip in the bath being about 30 seconds. This gave good infiltration into the porous niobium, the remainder of the process being carried out as described above.

In the vanadium-gallium (V₃Ga) embodiment, vanadium powder is rolled, as above described, to produce a porous vanadium strip which is thereafter sintered in furnace 14 and passed through molten bath 15 where

gallium is maintained at a temperature in the range of about 100°C, since gallium melts at 30°C, the thus gallium-infiltrated vanadium strip being processed as described above, with respect to the niobium-tin-embodyment as carried out by the FIG. 1 apparatus.

As also pointed out above, the amount of reaction of the infiltrate with the porous metal is related to the time and temperature of the diffusion processing step, the times and temperatures being established by series of tests.

It has thus been shown that the present invention provides a ductile and effective superconductive material formed from a porous infiltrated metal strip having interconnected filaments of a superconducting phase produced by a relatively simple and inexpensive process wherein the amount of infiltrated metal converted into the superconducting phase is controlled by the amount of deformation, and the time and temperature of the diffusion heat treatment. Thus, this invention has greatly advanced the state of the art.

While a particular apparatus and operation sequence has been illustrated for producing the novel superconductive material, it is not intended to limit the method of manufacture to the specifically disclosed operational sequence of the illustrated apparatus as modifications and changes will become apparent to those skilled in the art, and it is intended to cover in the appended claims all such modifications and changes as come within the spirit and scope of the invention.

What we claim is:

1. A method for manufacturing a ductile superconductive material containing interconnecting filaments of a superconducting phase which in the bulk has a critical field in excess of 100 kilogauss including the steps of: forming a porous metallic strip having a network of interconnecting pores from material selected from the group consisting of niobium and vanadium; sintering the thus formed porous metallic strip; infiltrating into interconnecting pores of the porous metallic strip a metallic material selected from the group consisting of tin, aluminum, germanium, antimony, gallium, and mixtures thereof by passing the metallic strip through a molten bath of the metallic material wherein the metallic material infiltrates into and substantially fills the pores of the metallic strip; reducing the thickness of the thus infiltrated porous metallic strip up to about 75 percent by passing the strip through a thickness reducing mechanism; and diffusion heat treating the thus infiltrated metallic strip thereby creating interconnecting filament of a superconducting phase of a compound formed by the reaction of the porous metallic strip and the infiltrated metallic material.

2. The method defined in claim 1, wherein the step of forming the metallic strip is accomplished by compacting finely powdered metallic material into a strip.

3. The method defined in claim 1, wherein the step of forming the metallic strip is accomplished by compacting hydrides of selected metallic material into a strip, the hydrides decomposing to form the porous metallic strip during the sintering step.

4. The method defined in claim 1, wherein the step of diffusion heat treating the thus infiltrated metallic strip is accomplished by passing same through a diffusion heat treating furnace wherein at least a portion of

the metallic material is reacted with the porous metallic strip.

5. The method defined in claim 1, additionally including the step of collecting the diffusion heat treated metallic strip by rolling same on a collecting apparatus.

6. The method defined in claim 1, wherein the step of forming the porous metallic strip is accomplished by containing niobium powder of a particle size in the range of -100 to -400 mesh, and directing the thus contained niobium powder through a compacting roller apparatus forming a continuous "green" strip of porous niobium.

7. The method defined in claim 6, wherein the step of sintering is accomplished by passing the porous niobium strip through a sintering furnace having an atmosphere selected from the group consisting of vacuum and inert gas, a temperature in the range of 1,850°C to 2,250°C, and for a time period of about 3 minutes.

8. The method defined in claim 6, wherein the step of infiltrating the porous niobium strip is accomplished by passing the strip through a bath of molten tin having a temperature range of 500°C to 1000°C and for a time period ranging from less than 1 minute to about 3 minutes.

9. The method defined in claim 7, wherein the step of thickness reduction of the tin-infiltrated strip is accomplished by passing the strip through a rolling apparatus whereby the thickness of the strip is reduced in the order of up to 75 percent.

10. The method defined in claim 9, wherein the step of diffusion heat treating the tin-infiltrated strip is accomplished by directing the strip through a diffusion heat treating furnace having a temperature in the range of 925°C to 1,075°C for a time period varying from less than 1 minute to several hours depending on the amount of infiltrated tin to be converted to Nb₃Sn.

11. The method defined in claim 1, wherein the porous metallic strip constitutes a porous niobium strip, wherein the step of infiltrating the niobium strip is accomplished by directing the strip through a molten bath selected from the group consisting of tin, aluminum, antimony, germanium and mixtures thereof, and wherein the diffusion heat treating of the infiltrated niobium strip creates a superconductive material containing interconnecting filaments of a superconducting phase selected from the group consisting of Nb₃Sn, Nb₃Al, Nb₃(Al,Ge), and Nb₃Sb.

12. The method defined in claim 1, wherein the porous metallic strip constitutes a porous vanadium strip, wherein the step of infiltrating the vanadium strip is accomplished by directing the strip through a molten bath, selected from the group consisting of gallium, aluminum, germanium, and mixtures thereof, and wherein the diffusion heat treating of the infiltrated vanadium strip creates a superconductive material containing interconnecting filaments of superconducting phase selected from the group consisting of V₃Ga, V₃Al, and V₃(Al,Ge).

13. The method defined in claim 1, wherein the step of diffusion heat treating is accomplished by coiling the thus infiltrated strip, and subjecting the thus coiled strip to a diffusion heating means.

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