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[54] METHOD FOR PRODUCING SUPERCONDUCTING WIRE AND PRODUCTS OF THE SAME

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[57] ABSTRACT

A method for producing a composite superconducting wire including one or more strands of high-field Type II superconductor embedded in a conductive matrix of normal material and the product of the said method. A composite body is prepared which includes a matrix in which are embedded one or more rods of a metal which is capable of forming a high-field Type II superconductor upon high temperature extruded to an intermediate diameter, and then is hot-drawn to a final diameter at temperatures exceeding about 100°C, by multiple passes through drawing dies, the composite being reduced in cross-sectional area approximately 15 to 20% per draw. In a preferred mode of practicing the invention, the rods comprise vanadium or niobium, with the matrix being respectively gallium-bronze or tin-bronze, and the superconductive strands being formed by high temperature diffusion of the gallium or tin into the rods subsequent to drawing.

12 Claims, No Drawings

METHOD FOR PRODUCING SUPERCONDUCTING WIRE AND PRODUCT OF THE SAME

BACKGROUND OF THE INVENTION

This invention relates generally to the field of superconductivity, and more specifically relates to the method for manufacture of composite superconducting wire and the resulting product.

Composite superconducting wire characterized by multiple longitudinally extending strands of high-field superconducting alloy in a surrounding matrix of copper or similar good thermal conductor, has found increasing application for use in the coils of superconducting magnets capable of producing extremely high magnetic fields.

Composite superconducting wire of the foregoing type is typically produced by initial preparation of a billet comprised of a copper extrusion can which contains a plurality of close-packed hexagonally-formed rod inserts. Each such rod insert may typically consist of a central round rod of a Type II superconductor, such as a niobium-titanium alloy, surrounded by one or more concentric tubes of high purity OFHC copper, the unit being drawn to a cohesive hexagonal bar before insertion into the extrusion can. The can containing the packed rods is suitably sealed at its ends and thereupon subjected to extrusion or swaging and drawing operations, which gradually reduce the diameter of the billet and of the contained inserts. The final very small diameter fine wire achieved by this technique contains the individual strands of the superconductor alloy in the surrounding copper matrix. The drawing operations cited are, for reasons to be set forth below, conducted at room temperature, and during the course of such mechanical working of the said billet, annealing may be required between draws, in order to remove the effects of cold work and maintain the required ductility for additional reduction in area.

In the case of several of the more significant highfield Type II conductors, the procedure outlined above may not be readily employed. In particular, intermetallic compounds such as V_3Ga and Nb_3Sn, which are among the presently recognized more useful Type II superconductors, are so brittle in nature, that the drawing processes are ineffective in working them. Indeed, taking recognition of this problem, it has been proposed to prepare composite superconducting wire based upon such high-field intermetallic Type II superconductors, by preparing a billet structure similar to that described above, but utilizing as the rod inserts a central core of vanadium or niobium surrounded by a matrix of Ga-bronze or of Sn-bronze. Pursuant to this approach the billet is appropriately reduced, in a manner similar to that indicated for the Nb-Ti composite wire, and after the desired fine diameter composite wire is achieved, the resultant product is subjected to a prolonged heating schedule — which serves to diffuse the gallium or tin into the central conductor to form the desired superconducting alloy thereat.

Pursuant to the foregoing procedures, it will be appreciated that sound reasons are present for supposing that the drawing operations shall usually be conducted at room temperature. In particular, it is known that in the case of a Type II superconductor, the strength of the attainable magnetic field when such wire is used in an electro-magnet is limited, because the superconducting state of the winding is impaired at a critical current by its own magnetic field. The transition of the coil to the normal state, furthermore, occurs at much smaller critical current than that corresponding to the upper critical field. Such result obtains because of interaction of the flux lines created in the wire by the magnetic field, and the current by which the coil is operated. In particular, the Lorentz force acting on a flux line is such that if such line is not pinned to the wire, it will start to move, generating localized heating which may initiate transition to the normal state. Aside from the use in composite wires of a highly conductive matrix of normal material to minimize such localized heating, it is known that lattice imperfections introduced by plastic deformation, and inhomogeneities in alloy composition, are capable of providing pinning sites that restrain movement of the flux lines. Cold-working techniques utilized in accordance with the foregoing processes serve to generate the desired lattice imperfections thereby providing pinning sites.

In the case where the rods of the composite body are an alloy-type material, such as Nb-Zr or Nb-Ti, encased in a pure copper matrix, the requirements for annealing are not too stringent. Where, however, it is desired to obtain intermetallic compounds such as V_3Ga or Nb_3Sn, much more difficult problems occur. In particular, it unfortunately is true that the Ga-bronze or Sn-bronze matrices present in the composites being drawn, work-harden very rapidly. Therefore, the composite being worked will typically require intermediate annealing after each two or three draws or every 40% reduction in cross-sectional area where cold-drawing is indeed utilized. This requirement for frequent "annealing" must furthermore be viewed in the context of the overall operation being conducted, if its full detrimental impact is to be appreciated. Indeed the complex process of producing small diameter multifilament superconducting wire of which the annealing is but a part, includes the steps of wire-drawing, placing the wire in an annealing furnace, annealing the wire in an inert atmosphere for a period of time, cooling the wire in a manner to prevent surface oxidation, stringing the annealed wire through a wire-drawing machine, drawing the wire, and then repeating the entire operation after the material has work hardened. Accordingly, it will be appreciated that the time required where annealing must be effected every two or three draws, together with the attendant expense, renders a process such as this completely economically prohibitive for practical production operations.

In accordance with the foregoing, it may be regarded as an object of the present invention, to provide a method for manufacture of composite superconducting wire based upon high-field Type II superconductors resulting in a superior product, whereby the time required for reducing a composite billet to a desired cross-section is vastly reduced, with commensurate saving in attendant expense.

It is a further object of the present invention, to provide a method for drawing a composite billet including rods of metal to be formed into high-field Type II superconducting strands, whereby work-hardening of the matrix containing the element to be alloyed with the rod is minimized during drawing of the composite material, and wherein the formation of adequate pinning sites in the ultimate superconductor product remains unimpaired.

SUMMARY OF INVENTION

Now, in accordance with the present invention, the foregoing objects, and others as will become apparent in the course of the ensuing specification, are achieved in a method according to which a composite billet is initially formed, consisting of a conductive matrix of normal material in which are embedded one or more rods of a metal which is capable of forming a high-field Type II superconductor upon high temperature reaction with a component of said matrix. The metallic rods are embedded in a matrix of copper, or other good thermal conductor such as silver or gold, containing in alloy the second element of the superconducting strands to be formed. The composite billet is extruded to an intermediate diameter, and thereafter drawn at temperatures over about 100°C and typically in the approximate range of 100° to 300°C, to a final diameter, by reducing the cross-sectional area approximately 15–20% per draw. The upper temperature limit is controlled by the stability of the wire drawing lubricant and ultimately by oxidation of the surface of the wire. By the utilization of high temperature lubricants such as molybdenum disulfide or graphite, and an inert gas shield, the composite can be drawn at approximately 600°C. The high-field superconductors, such as the intermetallic compounds V_3Ga and Nb_3Sn, are formed after drawing by high temperature reaction and diffusion. By utilizing the relatively hot drawing temperatures indicated, the drawing process may be effectively carried out without frequent intermediate annealing: in general such an anneal is required not more frequently than every 10 to 12 draws. Typically, for example, a pre-annealed 110-strand vanadium in Ga-bronze matrix wire (14.85% Ga overall) can be hot-drawn from 57 to 13 mils at 218°C with only one additional intermediate anneal. The resultant product is found to be essentially equivalent to wire formed from the same billet where such billet is cold-drawn.

DESCRIPTION OF PREFERRED EMBODIMENT

The initial stages of the method in accordance with the present invention may be substantially identical with methodology utilized in the prior art for preparation of composite superconducting wire. The primary requirement for the billet is that it include a conductive matrix of normal material which encases or surrounds longitudinally extending rods of a material which is capable of forming the desired high-field Type II superconductor upon high temperature reaction with a component of the matrix. The billet can be assembled in any practical manner, which will yield the aforementioned construction. For example, a body of the desired matrix alloy may be initially cast and longitudinal passages then formed therein by boring or drilling, with the rods thereupon being inserted within the passages to provide the desired billet construction.

Bronze alloys constitute the matrix material employed in this preferred embodiment. As used herein, a bronze matrix is defined as a copper based alloy containing the material which forms the desired high-field Type II superconductor as the principal added element.

In a typical procedure, a billet is initially prepared including a plurality of close-packed rods mounted within a bronze extrusion can, which billet is evacuated and sealed at both ends prior to extrusion and drawing. Methodology of this general type is disclosed at various places in the art, including, for example, in U.S. Pat. No. 3,618,205. Where the composite wire to be formed is of the preferred type, including multiple strands of a Type II high-field intermetallic compound superconductor in a bronze matrix, hexagonally-shaped metallic rods are initially prepared including one element of the superconductor material to be formed. The rods, in particular, comprise a central core of the metallic element contained within a surrounding tubular cladding of a bronze alloy, e.g., copper and the other element of the superconductor.

Assuming the superconductor strands to be formed are, for example, V_3Ga, the rods will consist of a core of vanadium surrounded by a tubular cladding of Ga-bronze, i.e., copper containing about 15% gallium. A plurality of such rods are thus close-packed (the rods are initially worked to a hexagonal cross-section) within the surrounding extrusion can, so that the resulting billet consists in the aggregate of, for example, vanadium rod cores surrounded by a matrix of Ga-bronze. Similarly where, for example, Nb_3Sn is to be formed, the initial billet will essentially comprise longitudinally extending elements of niobium encased within a matrix of Sn-bronze.

Billets of the type described above may be initially extruded at relatively elevated temperatures, e.g., on the order of 500°C, and may then be cold-drawn at room temperature to an intermediate diameter, from which point hot-drawing to a final desired diameter is accomplished. The conditions of drawing and the methodolity utilized is set forth in the following Examples:

EXAMPLE I

A 1.050 inch diameter extruded billet containing 110 strands of vanadium in a gallium-bronze (about 15% Ga by weight) matrix was cold drawn to 0.205 inch diameter using a reduction in area of about 13–20% per draw. Work-hardening of the matrix required annealing in an argon atmosphere for one hour at 500°C after every 2 or 3 draws.

The 0.205 inch wire was then drawn down to 8 mils in accordance with the method of this invention by the following schedule:

a. Hot-draw to 72 mils, drawing temperature 200°–221°C, annealed in an argon atmosphere for one hour at 500°C;

b. Hot-draw to 25 mils, same drawing temperature and annealing cycle as in (a);

c. Hot-draw to 10 mils, same drawing temperature and annealing cycle as in (a);

d. Hot-draw to 8 mils drawing temperature 200°–221°C.

Samples of this 8 mil V and Ga-bronze matrix wire were reacted at 600°C for 3, 4, 5, 6, 7 and 11 days in an argon atmosphere in order to form the desired intermetallic compound V_3Ga on the periphery of each strand. The 5 day reaction time gave the best performance, viz. a critical current of 11.17 amps at 79 kilo Gauss.

To determine critical current density required an accurate measurement of the V_3Ga reaction zone area. This area was derived from planimeter measurements made on photomicrographs of the center and the edge of a cross-section of this 8 mil diameter wire. The V_3Ga reaction zone area was calculated as the difference between the total strand area and the unreacted strand area. By multiplying the reaction zone area by the number of strands in the wire, the total V_3Ga reaction zone area is ascertained. In order to determine critical current density for a specific magnetic field level, divide the critical current at that level by the total V_3Ga reaction zone area.

By utilizing this procedure, the superconducting properties of this wire measured at the boiling point of He are at 79 K Gauss, critical current (Ic) 11.17 amps and critical current density (Jc) 4.31 × 10^5 amp/cm^2.

EXAMPLE II

A 0.205 inch diameter wire as produced in Example I above (that is cold-drawn from a 1.050 inch extruded billet) was drawn down to 13 mils in accordance with the method of this invention by the following schedule:

a. Hot-draw to 57 mils, drawing temperature 200°–218°C, annealed in an argon atmosphere for one hour at 500°C.

b. Hot-draw to 19.5 mils, same drawing temperature and annealing cycle as in (a);

c. Hot-draw to 13 mils, drawing temperature 200°–218°C.

Samples of this wire were annealed, mounted on graphite spools to be used for testing, and heated in vacuum for 120 hours at 600°C in order to form the intermetallic compound V_3Ga on the periphery of each strand. After this high temperature reaction, testing at the boiling point of helium was conducted.

Critical current density was again ascertained from planimeter measurements as hereinbefore described in Example I.

The superconducting properties of this wire measured at the boiling point of helium are:

a. At 79 K Gauss, critical current (Ic) 23 amps. and critical current density (Jc) 4.9 × 10^5 amp./cm^2;

b. At 40 K Gauss, critical current (Ic) 41 amps. and critical current density (Jc) 8.7 × 10^5 amp./cm^2

EXAMPLE III

Although for most practical application, multiple strand composite superconductive wire is preferred, the methodology of the invention is not limited to its use with multiple strand constructions.

For purposes of the present Example, a single strand niobium in 10% Sn, 90% copper, matrix billet was made by induction melting pure tin and OFHC copper in a graphite tube in an argon atmosphere, lowering a niobium rod into the center of the tube and cooling. After zone remelting the solidified bronze billet to eliminate bubbles and cavities, a billet 8.7 inches long and 0.558 inch diameter was obtained. The billet was homogenized at 500°C for two hours in argon and water quenched. It was then hot-drawn at 100° to 110°C from 0.558 inch to 0.140 inch diameter, with anneals (and quench) at 0.273 inch and 0.140 inch diameters. Resultant samples were then hot-drawn at 200°C from 0.140 inch to 0.010 inch diameter, with anneals at 20 mils, and mounted on graphite spools for high temperature reaction treatments. Various samples were then held at 900°C for 6.5, 8 and 10 hours in an argon atmosphere in order to form the desired intermetallic compound Nb_3Sn on the periphery of each strand. These samples had critical currents of 1.36, 2.07 and 3.51 amps at 79 kilo Gauss.

Good results in accordance with the invention are obtained when the drawing temperatures exceed about 100°C. Where the multi-strand composite product being formed is V_3Ga, a preferable operating range for drawing is from about 200° to 300°C although higher temperatures may indeed be utilized. When the composite product being formed is to be Nb_3Sn, a drawing temperature of about 100°C was proven to be satisfactory. Prior to drawing, the wire is typically preheated to a temperature close to that at which it will be drawn. This can be effected in any convenient manner, e.g., through use of inductive heating via an induction coil, by passage of the wire through a radiant tube, or so forth. A factor governing the upper temperature limit for this invention is the stability of the wire drawing lubricant employed during warm drawing. For example, if a low temperature lubricant is used, such as one with a petroleum base, these lubricants are stable up to about 300°C. Therefore, for obvious safety reasons the hot drawing temperature should be maintained well below this temperature. However, by the utilization of high temperature lubricants such as graphite or molybdenum disulfide, hot drawing temperatures up to approximately 600°C can be practiced. Therefore, the selection of a drawing lubricant is a controlling factor for determining the temperature at which hot drawing is conducted.

A commercial fatty acid base wire drawing lubricant was modified by adding 5% MoS_2. This modification permitted satisfactory hot drawing temperatures up to 350°C. When hot drawing was conducted above this temperature, the wire surface oxidized and the lubricant appeared to decompose. It is quite probable that by increasing the amount of MoS_2 a higher drawing temperature could be employed.

With respect to the formation of pinning sites, it is believed that hot drawing does not adversely affect the formation of such sites. It is well known that pinning sites are formed as the result of lattice imperfections created by cold work. Since the niobium and vanadium rod inserts have substantially higher tensile strength levels than the matrix material, what might be considered hot working for the matrix is still cold working for the inserts. Therefore, pinning sites are still induced into the inserts. Once induced, these sites remain as lattice imperfections after subsequent processing, such as hot drawing and high temperature diffusion.

The precise metallurgical theory that will explain the success of this invention is not known. However, the restoration of ductility by hot drawing with the concommittant reduced effect of work hardening can best be explained as a form of recovery. Recovery is defined on page 10 of the A.S.M. Metals Handbook, 1948 Edition, as the removal of residual stresses by localized plastic flow as the result of low-temperature annealing operations; performed on cold worked metals without altering the grain structure or strength properties substantially. The effect of recovery is that residual stresses imparted by cold work are greatly reduced, thereby permitting additional mechanical work without elaborate annealing procedures.

While the present invention has not particularly set forth in terms of specific embodiments thereof, it will be understood in view of the present disclosure, that numerous variations upon the invention are now enabled to those skilled in the art, which variations yet reside within the scope of the present teaching. Accordingly, the invention is to be broadly construed and limited only by the scope and spirit of the claims now appended hereto.

We claim:

1. A method for producing a composite superconducting wire including a high-field Type II superconducting strand embedded in a conductive metallic matrix of normal material, comprising the steps of:

assembling a composite body including a rod surrounded by said matrix, said rod comprising a metal which forms an intermetallic compound characterized as a high-field Type II superconductor upon high temperature diffusion reaction with an alloying element of said matrix;

extruding said composite to an intermediate diameter;

hot drawing said intermediate diameter composite to a final diameter by multiple passes through drawing dies at temperatures above about 100°C but below the diffusion temperature range within which substantial diffusion occurs between the alloying element of said matrix and the material of said rod, said composite being reduced in cross-sectional area appproximately 15 to 20% per draw; and

subjecting said composite at said final diameter to reaction at a high temperature within said diffusion temperature range for an extended period required for substantial diffusion of said matrix alloying element into said rod and the formation of a superconducting layer adjacent the interface between said matrix and said rod.

2. A method according to claim **1**, wherein said rod comprises a metal selected from the group consisting of niobium and vanadium.

3. A method in accordance with claim **2**, wherein said rods are multiple in number, whereby multi-strand superconducting wire is formed.

4. A method in accordance with claim **3**, wherein said rods comprise vanadium and wherein said matrix consists essentially of a bronze containing gallium as the principal alloying element.

5. A method in accordance with claim **4**, wherein said bronze contains about 15 weight percent gallium.

6. A method in accordance with claim **3**, wherein said rods comprise niobium and wherein said matrix consists essentially of a bronze containing tin as the principal alloying element.

7. A method in accordance with claim **6**, wherein said bronze contains about 10 weight percent tin.

8. A method in accordance with claim **1**, wherein said high-field Type II superconductor consists essentially of V_3Ga.

9. A method in accordance with claim **1**, wherein said high-field Type II superconductor consists essentially of Nb_3Sn.

10. A method in accordance with claim **1**, wherein said hot drawing step is conducted at temperatures in the range of about 100°C to about 600°C and the range within which substantial diffusion takes place is at least about 600°C.

11. A method in accordance with claim **10**, wherein said hot drawing step is conducted at temperatures in the range of about 100°C to about 300°C, and said diffusion step is carried out in a substantially inert environment.

12. A product by the process of claim **1**.

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