

Description

Field of the Invention

This invention pertains to methods for producing clad superconductive wire-like and ribbon-like bodies and to apparatus and systems that comprise such bodies.

Background of the Invention

From the discovery of superconductivity in 1911 to the recent past, essentially all known superconducting materials were elemental metals (e.g., Hg, the first known superconductor) or metal alloys (e.g., Nb₃Ge, probably the material with the highest transition temperature T_c known prior to 1986).

Recently, superconductivity was discovered in new class of materials. See, for instance, B. Batlogg, *Physica*, Vol. 126,275 (1984), which reviews the properties of superconductivity in barium bismuth lead oxide, and J. G. Bednorz and K. A. Muller, *Zeitschr. f. Physik B - Condensed Matter*, Vol. 64, 189 (1986), which reports superconductivity in lanthanum barium copper oxide.

Especially the latter report stimulated worldwide research activity, which very quickly resulted in further significant progress. The progress has resulted, inter alia, to date in the discovery that compositions in the Y-Ba-Cu-O system can have superconductive transition temperatures T_c above 77K, the boiling temperature of liquid N₂ (M. K. Wu et al, *Phys. Rev. Letters*, Vol. 58, March 2, 1987, page 908; and P. H. Hor, *ibid*, page 911). Furthermore, it has resulted in the identification of the material phase that is responsible for the observed high temperature superconductivity, and in the discovery of compositions and processing techniques that result in the formation of bulk samples of material that can be substantially single phase material and can have T_c above 90K (see the U. S. Patent application Serial No. 024,046, entitled "Devices and Systems Based on Novel Superconducting Material," filed by B. J. Batlogg, R. J. Cava and R. B. van Dover on March 10, 1987, which is a continuation-in-part of an application filed by the same applicants on March 3, 1987, which in turn is a continuation-in-part of application Serial No.001,682, filed by the same applicants on January 9, 1987).

The excitement in the scientific and technical community that was created by the recent advances in superconductivity is at least in part due to the potentially immense technological impact of the availability of materials that are superconducting at temperatures that do not require refrigeration with expensive liquid He. Liquid nitrogen is

generally considered to be a very convenient cryogenic refrigerant. Attainment of superconductivity at liquid nitrogen temperature was thus a long-sought goal which for a long time appeared almost un-

Although this goal has now been attained, there still exists at least one barrier that has to be overcome before the new oxidic high T_c superconductive materials can be utilized in many technological applications. In particular, techniques for forming superconductive bodies of technologically significant shape have to be developed.

The superconductive oxide material is readily produced in powder form, and has been processed by ceramic techniques into various shapes such as pellets, discs, and tori. A recently filed U. S. patent application Serial No. 025,913, entitled "Apparatus Comprising a Ceramic Superconductive Body, and Method for Producing Such a Body", filed March 16, 1987 by E. M. Gyorgy and D. W. Johnson, Jr. discloses techniques for making ceramic superconductive bodies having at least one relatively small dimension (5 μm-1 mm). Such filamentary and sheet-like bodies include thin rods, filaments, tapes, and sheets, which can be incorporated into a variety of apparatus such as Bitter magnets, transmission lines, rotating machinery, maglev vehicles, and fusion devices.

Perhaps the economically most significant application of prior art metallic superconductors (e.g., Nb₃Sn) is in the form of magnet wires. Magnets incorporating such wires can be found in many scientific laboratories and, inter alia, are to be used in the proposed giant particle accelerator, the so-called "Superconducting Supercollider". Prior art superconductive wires universally have a composite structure, with one or more superconductive filaments embedded in normal (i.e., non-superconductive) metal, typically copper. The normal metal serves several critical functions in such wires, among them provision of a by-pass electrical conduction path, provision of thermal conductive means in the event of local flux motion, and enhancement of the mechanical strength of the wire. European patent application EP A0171918, published February 19, 1986, discloses a method of making clad PbMo₆S₈ superconductor wire. The method involves filling a barrier metal (typically Ta) container with PbMo₆S₈-type compound and/or Pb, Mo and S-containing components, reduce the cross section of the thus formed composite body, and heat treat the resulting product under pressure in, typically, an inert atmosphere.

For an overview of some potential applications of superconductors see, for instance, B.B. Schwartz and S. Foner, editors, *Superconductor Applications: SQUIDS and Machines*. Plenum Press 1977. S. Foner and B.B.Schwartz, editors *Superconduc-*

for Material Science, Metallurgy, Fabrications, and Applications, Plenum Press 1981. Among the applications are power transmission lines, rotating machinery, and superconductive magnets for e.g. fusion generators, MHD generators, particle accelerators, levitated vehicles, magnetic separation, and energy storage. The prior art has considered these actual and potential applications in terms of the prior art (non-oxidic) superconductors. It is expected that many of the above and other applications of superconductivity would materially benefit if high T_c superconductive wire could be used instead of the previously considered relatively low T_c wire. We are disclosing herein techniques for producing such wire, as well as other bodies such as tape.

According to the present invention there is provided a method as defined in claim 1.

Disclosed is a method for producing elongate superconductive bodies in which the superconductive material is a sintered oxide, typically a cuprate, and is surrounded by a cladding, typically a normal metal. Cuprates of interest herein typically are of nominal composition $M_{3-m}M'_mCu_3O_{9-\delta}$, with M being preferably primarily Ba (substitution of all or some Ba by elements such as Ca and Sr is contemplated), M' being preferably one or more of Y, La, Eu, Lu and Sc, m being preferably 1, δ being typically in the range 1.5-2.5, and the divergence from the nominal formula amounts of M and M' being typically at most 10%. Currently preferred cuprates have nominal composition $Ba_2YCu_3O_{9-\delta}$ where δ is preferably about 2.1. This material will also be referred to as (Ba, Y) cuprate.

Such bodies are frequently referred to herein as "wires" or "tapes", respectively. This usage is not intended to imply any limitation, e.g. with regard to cross section of the wire-like bodies (for instance, such bodies may advantageously have noncircular cross section and may also comprise a multiplicity of coaxial superconductive bodies).

The inventive method comprises forming an intermediate body comprising a cladding material surrounding a quantity of oxide powder, forming an elongate body from the intermediate body by means of one or more cross section-reducing operations (e.g. one or more passes through wire drawing dies, or through rolling apparatus), and heat treating the elongate body.

Frequently the elongate body will be subjected to a shaping operation prior to the heat treatment, such that the elongate body is put into a form that substantially corresponds to the shape in which the body is to be used. For instance, the body may be wound helically on a mandrel into the shape of a magnet coil.

The intermediate body typically comprises a quantity of oxide powder surrounded by a diffusion

barrier which in turn is surrounded by a normal metal jacket. Exemplarily, the normal metal jacket is a copper tube, the diffusion barrier comprises a thin-walled silver tube inside a thin-walled Ni tube, and the oxide powder is packed into the silver tube. If the normal metal jacket material is inert with respect to the oxide then a diffusion barrier may not be required. Ag is such an inert metal, at least with regard to (Ba, Y) cuprate.

The heat treatment of the elongate body is carried out such that substantial sintering of the oxide powder occurs, and such that, after completion of the heat treatment, the chemical composition of the sintered powder is within predetermined limits that are associated with the occurrence of superconductivity in the sintered oxide powder or an unclad sintered oxide body produced from the powder.

The oxides of concern herein are relatively unstable with regard to their oxygen content (e.g., they can readily lose oxygen when heated to some relatively high temperature) and are superconductive only within a relatively narrow range of oxygen content. Therefore, the invention requires that measures be taken to insure that, upon completion of the heat treatment, the oxygen content of the sintered material is such that the material becomes superconductive at a technologically significant temperature, typically $> 77K$. Among such measures are hermetic sealing of the intermediate body at ambient or higher oxygen partial pressure, optionally together with placement of oxygen donor material (e.g., BaO_2 or AgO) inside the diffusion barrier, or introduction of oxygen into the space inside the diffusion barrier directly through the powder material, or possibly through a perforated tube placed axially inside the barrier or through perforations in the normal metal cladding.

The inventive method can be used to, inter alia, produce monofilament or multifilament superconductive wire of a variety of cross sectional shapes, or to produce tape or ribbon containing one or more superconductive elements. Many systems as well as apparatus can advantageously comprise wire or tape according to the invention. The availability of these superconductive bodies typically will make possible operation at a higher temperature than would be possible with prior art superconductive wire. Exemplary of apparatus that advantageously comprises inventive wire or tape is a superconductive solenoid, and exemplary of such systems is a particle accelerator, a maglev transportation system, a fusion reactor with magnetic confinement, and a power transmission line. Inventive bodies may also be used as signal transmission lines in electronic apparatus.

Preferred embodiments become superconductive at a temperature $T_c > 77K$. An example of a

material with $T_c > 77K$ is $Ba_2YCu_3O_{8.9}$. There have recently been reported claims that indications of superconductivity have been observed above 200K, at temperatures as high as 240K, in some oxides (cuprates) of the type that is of concern herein. See, for instance, New York Times, Saturday March 28, 1987, page 6, which reports on observations made at Wayne State University. See also J. T. Chen et al, "Observation of the Inverse ac Josephson Effect at 240K", to be published. Similar claims have also been made by workers at Berkeley University. The inventive method for making elongate oxide superconductive bodies comprising a normal metal cladding is broadly applicable to forming such bodies from oxide powder and is, in particular, applicable to forming such bodies from cuprate powders such as the (La, Y) cuprate on which the Wayne State and Berkeley experiments were done.

Brief Description of the Drawings

FIGS. 1 and 2 show schematically in end view exemplary monofilament and multifilament inventive wire, respectively;

FIG. 3 similarly depicts an exemplary inventive tape;

FIG. 4 schematically shows wire according to the invention shaped into a helical coil;

FIG. 5 schematically depicts a superconductive magnet; and

FIG. 6 shows the resistance as a function of temperature of a clad superconductive oxide body according to the invention.

Detailed Description of Some Preferred Embodiments

For reasons similar to those given above for prior art superconductive wires, wires and tapes based on superconductive oxide also advantageously are composite bodies that comprise normal metal cladding that surrounds the superconductive oxide body or bodies. A reason for embedding the superconductive oxide body in a normal metal that is not present in prior art wires is the need to substantially eliminate interaction of the superconductive material with the environment. We have found, for instance, that the oxygen content of some cuprate powders in air can decrease with time even at room temperature. Such decrease can impair the superconductive properties of the material. Furthermore, the possibility of adverse reaction with water vapor, CO_2 , and other environmental gases exists. A still further reason is the need for mechanical support of the generally relatively brittle sintered oxide body such that the body can withstand the Lorentz forces due to the interaction

of the current through the body and the magnetic field created by the current.

FIG. 1 schematically depicts the end view of an exemplary wire (10) according to the invention, in which 11 is the sintered oxide superconductive filament, 12 is the normal metal (e.g., Cu) jacket, 13 and 14 are the two layers of a diffusion barrier, where 13 is a material (e.g., Ag, Au, Pd) that is relatively inert with respect to oxygen and the other constituents of the oxide, and 14 is a material that substantially does not form an alloy with the material of 12 as well as with the material of 13. If 12 is Cu and 13 is Ag, then 14 can advantageously be Ni.

FIG. 2 similarly depicts schematically the end view of an exemplary multifilament wire (20), in which each of three sintered oxide filaments 21 is surrounded by a diffusion barrier 23, and is embedded in normal metal 22. A further exemplary embodiment (not shown) comprises a superconductive oxide filament surrounded by a dielectric layer which in turn is surrounded by a tubular superconductive oxide body, (possibly with diffusion barriers where needed) with this coaxial assembly being surrounded by normal metal cladding.

FIG. 3 schematically depicts an inventive tape 30, with 31 being the sintered oxide body, 33 the diffusion barrier, and 32 the normal metal jacket. Another exemplary inventive tape (not shown) contains a multiplicity of ribbon-like superconductive bodies embedded in a normal metal cladding.

A significant aspect of the invention is processing that results in a normal metal-clad oxide superconductive body or bodies (filament(s), ribbon(s)) having technologically significant superconductive properties. Among the most important of these properties is the transition temperature T_c (herein considered to be the highest temperature at which the DC resistance is zero to within measurement limits). Desirably $T_c > 77K$. Furthermore, the transition temperature of the composite clad body is desirably close to (preferably no less than 90% of) the transition temperature of a bulk ceramic body of essentially the same composition.

The processing is a multistep procedure that typically comprises some or all of the steps below. The oxide starting material can be produced by a known process that exemplarily comprises mixing metallic oxides, hydroxides, carbonates, hydrates, oxalates or other reactive precursors with a lubricating liquid in the appropriate ratio to obtain the desired final composition, filtering and drying the slurry, fragmenting the dried cake, and calcining the fragments in an O_2 -containing atmosphere (exemplarily heating to $900^\circ C$, 2 hours at temperature, furnace cool). The calcined fragments are again milled, re-fragmented and fired, as needed to achieve homogeneity. The homogeneous ma-

terial is then fragmented to produce a powder of the desired mesh size.

The thus produced powder optionally is heat treated (typically 300-700 °C, 10 minutes - 2 hours, O₂ partial pressure 0.1-10 atm, and/or is optionally mixed with oxygen donor powder (e.g., finely divided silver oxide such as AgO) or grain growth inhibitor (Ag powder). The powder is then packed into a container that comprises the normal metal (e.g., Cu, Ag, maraging steel) outer jacket and, optionally, one or more diffusion barriers (e.g., Ni and Ag). The outer jacket surface may be protected against oxidation by means of a layer of appropriate material (e.g., Ag). The container is then closed (e.g., pinched off or welded), or loss of oxide powder prevented by other appropriate means, and subjected to some appropriate cross section-reducing step(s) such as drawing through a series of dies, or rolling, swaging or extruding, either at room temperature or at some other (typically elevated) temperature. The thus produced elongate composite body is then optionally subjected to a shaping operation (e.g., wound on a mandrel into a coil shape).

The (shaped or unshaped) elongate body is then heat treated to result in substantial sintering of the oxide powder. The currently preferred heat treatment typically comprises heating the body to a temperature in the range 700-950 °C, maintaining it at that temperature until substantial sintering has taken place (exemplarily 0.1-100 hours), relatively slow cooling to a temperature in the range 300-700 °C, and maintaining it at that temperature until the desired oxygen concentration is established in the sintered material (exemplarily 1-24 hours).

If the composite body comprises precipitation-hardenable normal metal (e.g., maraging steel) then the above heat treatment advantageously is followed by a known precipitation hardening treatment.

The need to embed the oxide body in normal metal, together with the tendency of the relevant oxides to lose oxygen at relatively high temperatures (and to take up oxygen at somewhat lower temperatures) requires novel processing features. Among these features typically is the need to prevent contact of the powder with material that can oxidize at temperatures encountered during processing. The currently preferred technique for preventing such contact is to surround the oxide with a thin layer of an appropriate non-reactive material, e.g., Ag or Au. Various materials such as Pd, Ru, Rh, Ir, Os, Pt, Ni, and stainless steel may also be useful under some circumstances. We refer to this layer as the diffusion barrier.

Under some circumstances, inventive wire (or tape) need not comprise a diffusion barrier. For instance, if the normal metal jacket consists of

metal that is substantially inert with respect to oxygen and does not "poison" the oxide then no diffusion barrier is required. We have discovered that, at least for (Ba, Y) cuprate, Ag is such a normal metal.

Novel processing features are also occasioned by the need to maintain the oxygen content of the sintered powder within a relatively narrow range. Sintering of the oxide particles is frequently carried out at temperatures above about 700 °C. We have observed that at such temperatures under ordinary pressure the oxides of interest herein frequently lose oxygen. Thus, the inventive method typically comprises features designed to prevent the loss of the freed oxygen from the powder-containing space. Exemplarily this is accomplished by hermetic sealing of the elongate body prior to the heat treatment, possibly in a high O₂-pressure environment, by connecting a high pressure O₂ reservoir to the ends of the elongate body during heat treatment, or by carrying out the heat treatment in relatively high pressure (e.g., 2-20 atm) oxygen. In the latter case oxidation of the normal metal surface has to be prevented. Thus, either the normal metal jacket consists of relatively inert material (e.g., Ag), or the surface of the jacket is coated with a relatively inert material (e.g., Ag, Au, or Pd).

Instead of, or in addition to, measures designed to prevent loss of O₂ from the space occupied by the oxide powder, the inventive method may also comprise measures designed to introduce O₂ into that space. Exemplarily this can be done by forcing a flow of O₂ through the space, or, preferably, by introducing an oxygen donor material (e.g., BaO₂ or AgO powder) into the space. Such donor material releases oxygen during heat treatment, with the released oxygen then being available for incorporation into the superconductive oxide. It will be appreciated by those skilled in the art that a material, in order to be useful as an oxygen donor must not be a poison of the superconductive oxide, i.e., react with the oxide in a manner that substantially impairs its superconductive properties.

In some cases it may be possible to place a perforated tube into the powder space of the intermediate body, such that, after carrying out the size-reducing operation, a perforated channel exists through the powder. Through this channel O₂ can then easily be supplied. In some cases, it may be advantageous to perforate, at appropriate intervals, the normal metal that surrounds the oxide powder, and to contact the perforated elongate body with oxygen during the heat treatment.

As indicated above, the superconductive oxides frequently give up oxygen when heated to a relatively high temperature (e.g. about 900 °C) in ambient air or in moderate (e.g., 1 atmosphere) O₂

pressure. On the other hand, these oxides frequently take up oxygen upon cooling to intermediate temperatures. This thermodynamic property of the oxide may form the basis of a novel heat treatment in which the oxygen partial pressure over the oxide powder is adjusted such as to maintain optimum oxygen stoichiometry during the heat treatment. Although the details of the treatment depend frequently on the composition of the powder as well as the temperature, it can be said that in the novel variable O_2 -pressure heat treatment the (relatively high temperature) sintering step typically is carried out at a relatively high (e.g., 1.5-20 atm) O_2 partial pressure, and the subsequent (relatively low temperature) step is carried out at a relatively low (e.g., 1-5 atm) O_2 partial pressure, with a slow cool from the high to the low temperature being currently preferred.

As will be appreciated by those skilled in the art, the temperature at which a particular heat treatment step is carried out depends inter alia on the length of the treatment step. Thus, the sintering can be carried out at a relatively low temperature (e.g., 700 °C) if the sintering time is relatively long (e.g., > 24 hours). Typically the sintering temperature is in the range 600-1100 °C, and the time from 0.1 to 1000 hours. The length and temperature of the sintering step typically also depend on the size of the oxide particles, with smaller particles making possible shorter time and/or lower temperature, due to the increased thermodynamic driving force for the sintering process. It is thus currently considered advantageous to use relative small particle size powders (e.g., < 5 μm , preferably < 2 μm , more preferably < 0.5 μm , average diameter) in the practice of the invention.

The oxide powders used in the practice of the invention advantageously have stoichiometric composition. By this we mean herein that they have a composition that is associated with high temperature superconductivity in bulk ceramic bodies produced from such powders. We have discovered that in at least some cases the partitioning (e.g., ball milling) process that is used to produce particles of the desired mesh size may, in addition to straining the material, result in a change in composition. For this reason, it may in some circumstances be desirable to subject the properly sized powder to a relatively low temperature (e.g., 300-700 °C) oxygen anneal (exemplarily 0.1-10 atm of O_2) for about 10 minutes - 2 hours prior to compacting the powder into the intermediate body.

As indicated above, in many cases it is desirable to shape the elongate clad body that is produced from the intermediate body by some appropriate known cross section-reducing process prior to heat treating the elongate body. The heat treatment typically results in sintering of the oxide pow-

der and therefore typically reduces the formability of the superconductive element. On the other hand, the heat treatment frequently results in softening of the normal metal component(s) of the elongate body. In order to produce inventive bodies having both formability prior to sintering and good mechanical strength, it is frequently desirable to use precipitation hardenable normal metal as cladding material. As is well known, such alloys (e.g., maraging steel, or Cu-Ni-Sn spinodal alloy) can be hardened by means of a relatively low temperature treatment after wire drawing and shaping. Such treatment typically does not affect the superconductive properties of the sintered oxide element(s). If applied to a properly shaped superconductive wire or tape (e.g., a helical coil) it can result in an article that can be readily handled and further processed.

Example I:

Powder (approximately 2.5 μm average particle size) of nominal composition $Ba_2YCu_3O_{6.9}$ was produced by a known process and subjected to a 600 °C, 15 minutes anneal in 1 atm of O_2 . A bulk body produced from the thus prepared powder has $T_c(R=0)$ of about 93 K. A silver tube (0.250 inches outside diameter, 0.030 inches wall thickness, was filled with the powder and the ends of the tube sealed. The thus produced preform was drawn down to 0.060 inches diameter in 15 passes at room temperature. The resulting wire was wound into a coil on a 1.5 inch diameter mandrel. At this stage the coil does not exhibit superconductivity. The coil was then heat treated as follows: heated to 900 °C, maintained at 900 °C for 8 hours; furnace cooled to 600 °C, maintained at 600 °C for 4 hours; furnace cooled to about 350 °C. All of this treatment was carried out in about 1 atm of flowing O_2 . The coil was then removed from the furnace, and a portion tested by standard DC-resistance measurement. The results of this measurement are given in FIG. 6. As can be seen, the wire was fully superconducting at 91 K. The sintered oxide was removed from a portion of the coil, powdered and analyzed by a standard powder X-ray technique. The spectrum of the material was essentially the same as that of a sintered bulk sample of composition $Ba_2YCu_3O_{6.9}$.

Example II:

A coil is prepared substantially as described in Example I, except that a 3/16 inch OD, 1/8 inch ID copper tube is used. A diffusion barrier was formed by first wrapping 0.002 inch thick Ni foil into the tube, followed by similarly wrapping 0.002 inch thick Au foil into the tube. The thus formed normal

metal jacket is then filled with powder. A portion of the wire is measured. The superconductive properties are substantially the same as those of the wire of Example I.

Example III:

A coil was produced substantially as described in Example I, except that a 3/16 inch OD, 1/8 inch ID copper tube was used instead of the silver tube. No superconductivity above 77 K was observed in the coil.

Example IV:

A coil was prepared substantially as described in Example I. After winding of the coil but prior to heat treating the coil, the Ag clad is perforated at intervals of about 1 inch. The heat treated coil was superconductive, with $T_c(R=0)$ about 91 K.

Example V:

A coil was prepared substantially as described in Example II, except that 0.002 inch Pt foil was used instead of the Au foil. A portion of the wire was measured and showed a broad transition to a low resistance state, terminating at about 30 K.

Example VI:

A tape is prepared substantially as described in Example I, except that the sealed, powder-filled Ag tube is elongated by rolling to 0.010 inch thickness in a standard rolling mill.

Example VII:

A coil is prepared substantially as described in Example I except that AgO powder (about 1.3 μm average particle size) is mixed with the cuprate powder (20% b.w. AgO). The coil has a superconductive transition substantially as shown in FIG. 6.

Claims

1. Method of producing an elongate body that comprises superconducting oxide material of a predetermined composition,

CHARACTERISED IN THAT the method comprises

- a) forming an intermediate body comprising a normal metal cladding surrounding a quantity of oxide powder and in contact therewith, the oxide powder comprising powder of composition that differs from said predetermined composition at most with respect to oxygen;

b) forming an elongate body from the intermediate body by means of one or more cross-section-reducing operations;

c) heat treating the elongate body such that substantial sintering of the oxide powder occurs, with the oxide powder being in contact with an appropriate quantity of oxygen during at least a part of step c) such that the thus produced body manifests superconductivity, with T_c of 77K or above, wherein at least the portion of the cladding that is in contact with the oxide powder comprises normal metal that is substantially inert with respect to oxygen and with respect to the oxide powder under the heat treating conditions; wherein

d) the predetermined nominal composition is $M_{3-m}M'_m\text{Cu}_3\text{O}_{8-\delta}$, where m is 1, δ is in the range 1.5-2.5, the divergence from the nominal formula amounts of M and M' is at most 10%, M is one or more elements selected from Ba, Ca and Sr, and M' is one or more elements selected from Y, La, Eu, Lu and Sc.

2. Method of claim 1, wherein the oxide powder is a cuprate powder of nominal composition $\text{Ba}_2\text{YCu}_3\text{O}_x$.
3. Method of any of claims 1-2, wherein the cladding comprises a diffusion barrier, with at least the portion of the diffusion barrier that is in contact with the oxide powder comprising normal metal that is substantially inert with respect to oxygen and with respect to the oxide powder under the heat treating conditions.
4. Method of claim 3, wherein at least the portion of the diffusion barrier comprises material selected from Ag and Au.
5. Method of claim 1, wherein the cross-section-reducing operation comprises wire drawing, swaging, extrusion, or rolling.
6. Method of claim 1, where heat treating comprises
 - i) maintaining the elongate body at a temperature in the range from about 700 to about 950 °C for a time in the range from about 0.1 to about 1000 hours; and
 - ii) maintaining, during at least a part of the heat treatment, at least a portion of the cuprate powder in contact with an appropriate quantity of oxygen such that, upon completion of the heat treatment, the oxygen content of at least a portion of the sintered cuprate powder corresponds to

metal jacket is then filled with powder. A portion of the wire is measured. The superconductive properties are substantially the same as those of the wire of Example I.

Example III:

A coil was produced substantially as described in Example I, except that a 3/16 inch OD, 1/8 inch ID copper tube was used instead of the silver tube. No superconductivity above 77 K was observed in the coil.

Example IV:

A coil was prepared substantially as described in Example I. After winding of the coil but prior to heat treating the coil, the Ag clad is perforated at intervals of about 1 inch. The heat treated coil was superconductive, with $T_c(R=0)$ about 91 K.

Example V:

A coil was prepared substantially as described in Example II, except that 0.002 inch Pt foil was used instead of the Au foil. A portion of the wire was measured and showed a broad transition to a low resistance state, terminating at about 30 K.

Example VI:

A tape is prepared substantially as described in Example I, except that the sealed, powder-filled Ag tube is elongated by rolling to 0.010 inch thickness in a standard rolling mill.

Example VII:

A coil is prepared substantially as described in Example I except that AgO powder (about 1.3 μ m average particle size) is mixed with the cuprate powder (20% b.w. AgO). The coil has a superconductive transition substantially as shown in FIG. 6.

Claims

1. Method of producing an elongate body that comprises superconducting oxide material of a predetermined composition,

CHARACTERISED IN THAT the method comprises

- a) forming an intermediate body comprising a normal metal cladding surrounding a quantity of oxide powder and in contact therewith, the oxide powder comprising powder of composition that differs from said predetermined composition at most with respect to oxygen;

b) forming an elongate body from the intermediate body by means of one or more cross-section-reducing operations;

c) heat treating the elongate body such that substantial sintering of the oxide powder occurs, with the oxide powder being in contact with an appropriate quantity of oxygen during at least a part of step c) such that the thus produced body manifests superconductivity, with T_c of 77K or above, wherein at least the portion of the cladding that is in contact with the oxide powder comprises normal metal that is substantially inert with respect to oxygen and with respect to the oxide powder under the heat treating conditions; wherein

d) the predetermined nominal composition is $M_{3-m}M'_mCu_3O_{9-\delta}$, where m is 1, δ is in the range 1.5-2.5, the divergence from the nominal formula amounts of M and M' is at most 10%, M is one or more elements selected from Ba, Ca and Sr, and M' is one or more elements selected from Y, La, Eu, Lu and Sc.

2. Method of claim 1, wherein the oxide powder is a cuprate powder of nominal composition $Ba_2YC u_3O_x$.
3. Method of any of claims 1-2, wherein the cladding comprises a diffusion barrier, with at least the portion of the diffusion barrier that is in contact with the oxide powder comprising normal metal that is substantially inert with respect to oxygen and with respect to the oxide powder under the heat treating conditions.
4. Method of claim 3, wherein at least the portion of the diffusion barrier comprises material selected from Ag and Au.
5. Method of claim 1, wherein the cross-section-reducing operation comprises wire drawing, swaging, extrusion, or rolling.
6. Method of claim 1, where heat treating comprises
 - i) maintaining the elongate body at a temperature in the range from about 700 to about 950°C for a time in the range from about 0.1 to about 1000 hours; and
 - ii) maintaining, during at least a part of the heat treatment, at least a portion of the cuprate powder in contact with an appropriate quantity of oxygen such that, upon completion of the heat treatment, the oxygen content of at least a portion of the sintered cuprate powder corresponds to





δ~2.1.

7. Method of claim 1 or 6, wherein the elongate body comprises oxygen donor material adapted for providing the appropriate quantity of oxygen or at least parts of that. 5
8. Method of claim 1 or 6, wherein the cladding has at least one orifice that permits access to the powder, and wherein heat treating comprises providing oxygen to the powder through the orifice. 10
9. Method of any of claims 1-8, further comprising a shaping operation carried out on the elongate body prior to the completion of heat treating. 15
10. Method of claim 9, wherein the shaping operation comprises forming a helical coil. 20
11. Method of any of claims 1-10, wherein the superconductive body is a monofilament or multifilament wire, or a monofilament or multifilament tape, or a coaxial wire. 25
12. Method of any of claims 1-11, wherein the cladding comprises a precipitation-hardenable normal metal, and wherein the method comprises a precipitation hardening step. 30
13. Method of any of claims 1-3 and 5-12, wherein the cladding material comprises Ag.
14. Method of claim 7, wherein the oxygen donor material is silver oxide, and the silver oxide is part of the quantity of oxide powder. 35
- Method of claim 1, wherein the intermediate body is sealed such that the quantity of oxide powder is not in contact with an atmosphere that surrounds the intermediate body and at least some of the oxygen being in contact with the oxide powder is provided by the quantity of oxide powder and or an oxygen donor material. 40
16. An article of manufacture comprising an elongate superconductive body according to any of the preceding claims 1-15. 45

Patentansprüche

1. Verfahren zur Herstellung eines gestreckten Körpers, der ein supraleitendes Oxidmaterial einer vorherbestimmten Zusammensetzung aufweist, dadurch gekennzeichnet, daß das Verfahren umfaßt: 55

a) Formen eines Zwischenkörpers, der einen normalen, der eine Menge an Oxidpulver umgebenden und damit in Kontakt damit stehenden Metallmantel aufweist, wobei das Oxidpulver ein Pulver einer Zusammensetzung umfaßt, das sich von der vorherbestimmten Zusammensetzung höchstens bezüglich des Sauerstoffes unterscheidet,
 b) Formen eines gestreckten Körpers aus dem Zwischenkörper mit Hilfe von einem oder mehreren querschnittsvermindernden Vorgängen;
 c) Wärmebehandlung des gestreckten Körpers, so daß ein beträchtliches Sintern des Oxidpulvers auftritt, wobei das Oxidpulver in Kontakt mit einer geeigneten Menge Sauerstoff zumindest während eines Teils von Schritt c) ist, so daß der derart hergestellte Körper Supraleitung mit einem T_c von 77 K oder darüber zeigt, wobei mindestens der Teil des Mantels, der in Kontakt mit dem Oxidpulver ist, ein normales Metall umfaßt, daß im wesentlichen inert bezüglich des Sauerstoffes und bezüglich des Oxidpulvers unter den Bedingungen der Wärmebehandlung ist; wobei
 d) die vorherbestimmte nominelle Zusammensetzung $M_{3-m}M'_mCu_3O_{9-\delta}$ ist, wobei m 1 ist, δ im Bereich 1,5-2,5 liegt, die Abweichung von den Nominalformelwerten von M und M' höchstens 10%, M ist eines oder mehrere unter Ba, Ca und Sr ausgewählte Elemente, und M' eines oder mehrere unter Y, La, Eu, Lu und Sc ausgewählte Elemente ist bzw. sind.

2. Verfahren nach Anspruch 1, worin das Oxidpulver ein Kupratpulver der Nominalzusammensetzung $Ba_2YCu_3O_x$ ist.
3. Verfahren nach einem der Ansprüche 1 bis 2, worin der Mantel eine Diffusionssperrschicht aufweist, wobei mindestens der Teil der Diffusionssperrschicht, der in Kontakt mit dem Oxidpulver ist, ein normales Metall umfaßt, das im wesentlichen inert bezüglich Sauerstoff und bezüglich des Oxidpulvers unter den Bedingungen der Wärmebehandlung ist.
4. Verfahren nach Anspruch 3, worin mindestens der Teil der Diffusionssperrschicht ein unter Ag und Au ausgewähltes Metall umfaßt.
5. Verfahren nach Anspruch 1, worin die querschnittsreduzierenden Vorgänge das Ziehen, Stauchen, Strangpressen oder Walzen umfassen.



6. Methode nach Anspruch 1, wobei die Wärmebehandlung aufweist:

1. Halten des gestreckten Körpers bei einer Temperatur im Bereich von ungefähr 700 bis ungefähr 950 °C für eine Zeit im Bereich von ungefähr 0,1 bis ungefähr 1000 Stunden; und

2. Halten während mindestens eines Teils der Hitzebehandlung, von mindestens einem Teils des Kupratpulvers in Kontakt mit einer geeigneten Menge an Sauerstoff, so daß nach Beendigung der Wärmebehandlung, der Sauerstoffgehalt von mindestens einem Teil des gesinterten Kupratpulvers einem $\delta \sim 2,1$ entspricht.

7. Verfahren nach Anspruch 1 oder 6, worin der gestreckte Körper Sauerstoffdonormaterial umfaßt, das die geeignete Menge an Sauerstoff oder zumindestens ein Teil davon zur Verfügung stellt.

8. Verfahren nach Anspruch 1 oder 6, worin der Mantel mindestens eine Öffnung besitzt, die einen Zugang zum Pulver erlaubt und worin das Wärmebehandeln die Versorgung des Pulvers mit Sauerstoff durch die Öffnung umfaßt.

9. Verfahren nach einem der Ansprüche 1 bis 8, das weiterhin einen Gestaltungsvorgang umfaßt, der mit dem gestreckten Körper vor der Beendigung der Wärmebehandlung ausgeführt wird.

10. Verfahren nach Anspruch 9, worin der Gestaltungsvorgang das Formen einer wendelförmigen Spule umfaßt.

11. Verfahren nach einem der Ansprüche 1 bis 10, worin der supraleitende Körper ein Monofilament- oder Multifilamentdraht ist, oder ein Monofilament- oder Multifilamentband, oder ein coaxialer Draht.

12. Verfahren nach einem der Ansprüche 1 bis 11, worin der Mantel ein abscheidungs-härtbares normales Metall aufweist, und worin das Verfahren einen Abscheidungs-Härtungsschritt aufweist.

13. Verfahren nach einem der Ansprüche 1 bis 3 und 5 bis 12, worin das Mantelmaterial Ag aufweist.

14. Verfahren nach Anspruch 7, worin das Sauerstoffdonormaterial Silberoxid ist und das Silberoxid Teil der Menge des

Oxidpulvers ist.

15. Verfahren nach Anspruch 1, worin der Zwischenkörper so abgedichtet ist, daß die Menge an Oxidpulver nicht in Kontakt mit der Atmosphäre ist, die den Zwischenkörper umgibt und mindestens einiger Sauerstoff, der in Kontakt mit dem Oxidpulver ist, von der Menge an Oxidpulver und/oder einen Sauerstoffdonormaterial zur Verfügung gestellt wird.

16. Gegenstand der einen gestreckten supraleitenden Körper umfaßt, hergestellt nach einem der vorhergehenden Ansprüche 1 bis 15.

Revendications

1. Procédé de fabrication d'un corps allongé qui comprend un matériau consistant en un oxyde supraconducteur ayant une composition prédéterminée,

CHARACTERISE EN CE QUE ce procédé comprend les opérations suivantes

a) on forme un corps intermédiaire comprenant une gaine en métal normal qui entoure une certaine quantité de poudre d'oxyde et qui est en contact avec celle-ci, la poudre d'oxyde consistant en une poudre dont la composition diffère de la composition prédéterminée, au moins en ce qui concerne l'oxygène;

b) on forme un corps allongé à partir du corps intermédiaire, par une ou plusieurs opérations de réduction de section transversale;

c) on applique un traitement thermique au corps allongé, de façon qu'il se produise un frittage notable de la poudre d'oxyde, avec la poudre d'oxyde en contact avec une quantité appropriée d'oxygène pendant au moins une partie de l'étape c), de façon que le corps ainsi produit soit supraconducteur, avec une température T_c de 77K ou plus, dans une condition dans laquelle au moins la partie de la gaine qui est en contact avec la poudre d'oxyde consiste en un métal normal qui est pratiquement inerte vis-à-vis de l'oxygène et vis-à-vis de la poudre d'oxyde, dans les conditions de traitement thermique; et en ce que

d) la composition nominale prédéterminée est $M_{3-m}M'_mCu_3O_{8-\delta}$, avec m égal à 1, δ dans la plage de 1,5-2,5, l'écart par rapport aux quantités nominales définies par la formule pour M et M' est au plus de 10%, M représente un ou plusieurs éléments sélectionnés parmi Ba, Ca et Sr, et M' représente un ou plusieurs éléments sélectionnés par-



mi Y, La, Eu, Lu et Sc.

2. Procédé selon la revendication 1, dans lequel la poudre d'oxyde est une poudre de cuprate de composition nominale $Ba_2YCu_3O_x$. 5
3. Procédé selon l'une quelconque des revendications 1 ou 2, dans lequel la gaine comprend une barrière de diffusion, au moins la partie de la barrière de diffusion qui est en contact avec la poudre d'oxyde consistant en un métal normal qui est pratiquement inerte vis-à-vis de l'oxygène et vis-à-vis de la poudre d'oxyde, dans les conditions de traitement thermique. 10
4. Procédé selon la revendication 3, dans lequel au moins la partie de barrière de diffusion consiste en un matériau sélectionné parmi Ag et Au. 15
5. Procédé selon la revendication 1, dans lequel l'opération de réduction de section transversale est une opération de tréfilage, de matriçage, d'extrusion ou de laminage. 20
6. Procédé selon la revendication 1, dans lequel le traitement thermique comprend :
 - i) le maintien du corps allongé à une température dans la plage allant d'environ 700 à environ 950 °C pendant une durée dans la plage allant d'environ 0,1 à environ 1000 heures; et 30
 - ii) le maintien, pendant au moins une partie du traitement thermique, d'au moins une partie de la poudre de cuprate en contact avec une quantité d'oxygène appropriée, de façon qu'à l'achèvement du traitement thermique, la teneur en oxygène d'au moins une partie de la poudre de cuprate frittée corresponde à $\delta \sim 2,1$. 35
7. Procédé selon la revendication 1 ou 6, dans lequel le corps allongé contient un matériau donneur d'oxygène qui est conçu pour fournir la quantité d'oxygène appropriée, ou au moins des parties de celle-ci. 40
8. Procédé selon la revendication 1 ou 6, dans lequel la gaine comporte au moins un orifice qui permet d'accéder à la poudre, et dans lequel le traitement thermique comprend l'application d'oxygène à la poudre à travers l'orifice. 45
9. Procédé selon l'une quelconque des revendications 1-8, comprenant en outre une opération de mise en forme qui est accomplie sur le corps allongé avant l'achèvement du traitement 50

thermique.

10. Procédé selon la revendication 9, dans lequel l'opération de mise en forme comprend la formation d'une bobine hélicoïdale. 55
11. Procédé selon l'une quelconque des revendications 1-10, dans lequel le corps supraconducteur est un fil monofilament ou multifilament, ou une bande monofilament ou multifilament, ou un fil coaxial. 60
12. Procédé selon l'une quelconque des revendications 1-11, dans lequel la gaine comprend un métal normal pouvant être durci par précipitation, et dans lequel le procédé comprend une étape de durcissement par précipitation. 65
13. Procédé selon l'une quelconque des revendications 1-3 et 5-12, dans lequel le matériau de gaine consiste en Ag. 70
14. Procédé selon la revendication 7, dans lequel le matériau donneur d'oxygène est de l'oxyde d'argent et l'oxyde d'argent fait partie de la quantité de poudre d'oxyde. 75
15. Procédé selon la revendication 1, dans lequel le corps intermédiaire est fermé hermétiquement de façon que la quantité de poudre d'oxyde ne soit pas en contact avec une atmosphère qui entoure le corps intermédiaire, et une partie au moins de l'oxygène qui est en contact avec la poudre d'oxyde est fournie par la quantité de poudre d'oxyde et/ou par un matériau donneur d'oxygène. 80
16. Un article manufacturé comprenant un corps supraconducteur allongé conforme à l'une quelconque des revendications 1-15 précédentes. 85