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FORM 1

SPRUSON & FERGUSON

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

APPLICATION FOR A STANDARD PATENT

LODGED AT SUB-OFFICE

30 MAR 1988

Sydney

American Telephone and Telegraph Company, incorporated in New York, of 550 Madison Avenue, New York, New York, 10022, UNITED STATES OF AMERICA, hereby apply for the grant of a standard patent for an invention entitled:

Apparatus and Systems Comprising a Superconductive Body, and Method for Producing Such Body

which is described in the accompanying complete specification.

Details of basic application(s):-

<u>Basic Applic. No:</u>	<u>Country:</u>	<u>Application Date:</u>
034117	UNITED STATES OF AMERICA	1 April 1987
036160	UNITED STATES OF AMERICA	6 April 1987

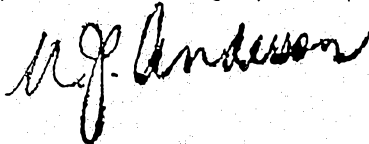
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DATED this THIRTIETH day of MARCH 1988

American Telephone and Telegraph Company

By:



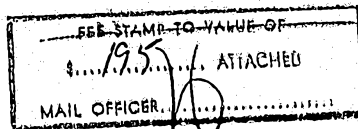
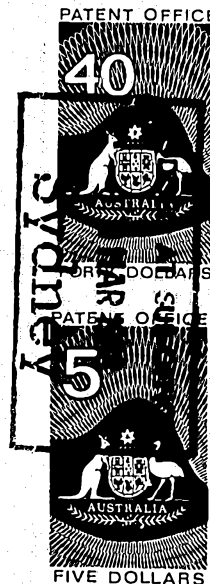
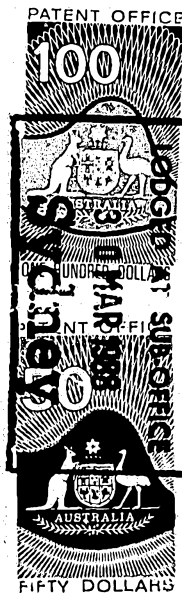
Registered Patent Attorney

TO: THE COMMISSIONER OF PATENTS
OUR REF: 53157
S&F CODE: 63845

5845/8

APPLICATION ACCEPTED AND AMENDMENTS

ALLOWED 20.11.89



COMMONWEALTH OF AUSTRALIAPATENTS ACT 1952-69DECLARATION IN SUPPORT OF A CONVENTION APPLICATION FOR A PATENT

In support of the Convention application made for a patent for an invention entitled: APPARATUS AND SYSTEMS COMPRISING A SUPERCONDUCTIVE BODY, AND METHOD FOR PRODUCING SUCH BODY I, Kenneth Graham Johnston of 30 Branscombe Gardens, Winchmore Hill, London N21 3BN, England do solemnly and sincerely declare as follows:

1. I am authorized by American Telephone and Telegraph Company, the applicant for the patent to make this declaration on their behalf.
2. The basic application(s) as defined by Section 141 of the Act were made in the United States of America on the 1st day of April 1987 and 6th day April 1987 ^{both} by Sungho Jin, Richard Curry Sherwood and Robert Bruce van Dover

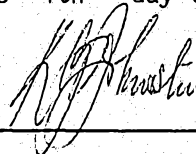
3. Sungho Jin of 145 Skyline Drive, Millington, New Jersey 07946, United States of America, Richard Curry Sherwood of 8 Vista Lane, New Providence, New Jersey 07974, United States of America, and Robert Bruce van Dover of 300 Emerson Lane, Berkeley Heights, New Jersey 07922, United States of America are the actual inventor(s) of the invention and the fact upon which American Telephone and Telegraph Company is entitled to make the application is as follows:

The said Company is the assignee of the actual inventor(s).

4. The ~~basic applications~~ ^{were} referred to in paragraph 2 of this declaration ~~was~~ the first ~~applications~~ made in a Convention country in respect of the invention ~~the~~ subject of the application.

Declared at LONDON

this 4th day of March 1988



Declarant

To: The Commissioner of Patents.

(12) PATENT ABRIDGMENT (11) Document No. AU-B-13893/88
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 593731

(54) Title
APPARATUS AND SYSTEMS COMPRISING A SUPERCONDUCTIVE BODY, AND METHOD FOR PRODUCING SUCH BODY

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(56) Prior Art Documents
AU 16693/88 H01B 12/00 C04B 35/00
AU 11422/88 H01B 12/00
AU 10014/88 H01L 39/14 H01B 12/00

(57) Claim

1. Method of producing an elongate superconductive body, CHARACTERIZED IN THAT the method comprises

- a) forming an intermediate body comprising a cladding surrounding a quantity of powder that comprises cuprate powder;**
- b) forming an elongate body from the intermediate body by means of one or more cross-section-reducing operations; and**
- c) heat treating the elongate body, the heat treatment comprising**
 - i) maintaining the elongate body above 700°C for a time such that substantial sintering of the cuprate powder occurs, and**
 - ii) maintaining, during at least a part of the heat treatment, at least a portion of the cuprate powder in contact with an oxygen-containing atmosphere, such that, after completion of the heat treatment, at least the portion of the cuprate powder manifests super conductivity at a temperature above 77K.**

2. Method of claim 1, wherein the cuprate powder has the general nominal formula $M_{3-m}M'_mCu_3O_{9-\delta}$, where m is about 1, δ is in the range 1.5-2.5,

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the divergence from the nominal formula amounts of M and M' is at most 10%, M is one or more elements selected from the group consisting of Ba, Ca, and Sr, and M' is one or more elements selected from the group consisting of Y, La, Eu, Lu, and Sc.

4. Method of any claims 1-3, wherein at least the portion of the cladding that is in contact with the powder consists essentially of normal metal that is substantially inert with respect to oxygen and with respect to the powder under the heat treating conditions.

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FORM 10

COMMONWEALTH OF AUSTRALIA

PATENTS ACT 1952

COMPLETE SPECIFICATION

(ORIGINAL)

FOR OFFICE USE:

Class Int Class

Complete Specification Lodged:
Accepted:
Published:

Priority:

Related Art:

This document contains the
amendments made under
Section 49 and is correct for
printing.

Name and Address
of Applicant:

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Complete Specification for the invention entitled:

Apparatus and Systems Comprising a Superconductive Body,
and Method for Producing Such Body

The following statement is a full description of this invention, including the
best method of performing it known to me/us

APPARATUS AND SYSTEMS COMPRISING A SUPERCONDUCTIVE BODY, AND METHOD FOR PRODUCING SUCH BODY

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.

5 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).

10 Recently, superconductivity was discovered in a new class of materials. See, for instance, B. Barlogg, 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
15 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
20 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
25 that can be substantially single phase material and can have T_c above 90K (see the Australian Patent Application No. 10014/88.



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 unreachable.

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 Australian patent application 13131/88.

(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., Nb_3Sn) 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.



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, Superconductor
5 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
10 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
15 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 of producing an elongate superconductive body, characterised in that the method comprises a) forming an intermediate body comprising a
20 cladding surrounding a quantity of powder that comprises cuprate powder; b) forming an elongate body from the intermediate body by means of one or more cross-section-reducing operations; and c) heat treating the elongate body, the heat treatment comprising i)
25 maintaining the elongate body above 700°C for a time such that substantial sintering of the cuprate powder occurs, and ii) maintaining, during at least a part of the heat treatment, at least a portion of the cuprate powder in contact with an oxygen-containing atmosphere, such that, after completion of the heat treatment, at
30 least the portion of the cuprate powder manifests super conductivity at a temperature above 77K.

An embodiment of the invention provides 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
35 herein typically are of nominal composition $M_{3-m}M'_m\text{Cu}_3\text{O}_{9-\delta}$, 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 about 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
5 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
10 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 embodiment method comprises forming an intermediate body
15 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.
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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 $Ba_2YCu_3O_{6.9}$. 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.

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;

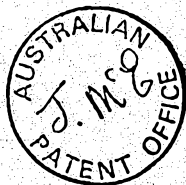
FIG. 4 schematically shows wire according to the invention shaped into a helical coil;

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.

5 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.

10 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
15 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
20 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.

25 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
30 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 $T_c > 77\text{K}$. Furthermore, the transition
35 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
5 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 O₂-
10 containing atmosphere (exemplarily heating to 900°C, 2 hours at temperature, furnace cool). The calcined fragments are again milled, re-fragmented and fired, as needed to achieve homogeneity. The homogeneous material 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
15 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
20 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
25 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-
30 950°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.

5 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
10 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.

15 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.

20 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
25 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
30 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).

35 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 O_2 through the space, or, preferably, by introducing an oxygen donor material (e.g., BaO_2 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 O_2 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 $900^\circ C$) in ambient air or in moderate (e.g., 1 atmosphere) O_2 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., $700^\circ C$) if the sintering time is relatively long (e.g., > 24 hours). Typically the sintering temperature is in the range $600-1100^\circ C$, 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., $< 5 \mu\text{m}$, preferably $< 2 \mu\text{m}$, more preferably $< 0.5 \mu\text{m}$, average diameter) in the practice
5 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
10 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., $300\text{-}700^{\circ}\text{C}$) oxygen anneal (exemplarily $0.1\text{-}10 \text{ atm}$ of O_2) for
15 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
20 treatment typically results in sintering of the oxide powder 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
25 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
30 tape (e.g., a helical coil) it can result in an article that can be readily handled and further processed.

Example I: Powder (approximately $2.5 \mu\text{m}$ average particle size) of nominal composition $\text{Ba}_2\text{YCu}_3\text{O}_{6.9}$ 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
35 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 O₂. 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 Ba₂YCu₃O_{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.

The claims defining the invention are as follows:

1. Method of producing an elongate superconductive body,
CHARACTERIZED IN THAT the method comprises

5 a) forming an intermediate body comprising a cladding surrounding a
quantity of powder that comprises cuprate powder;

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

c) heat treating the elongate body, the heat treatment comprising

10 i) maintaining the elongate body above 700°C for a time such that
substantial sintering of the cuprate powder occurs, and

ii) maintaining, during at least a part of the heat treatment, at least a
portion of the cuprate powder in contact with an oxygen-containing atmosphere,
such that, after completion of the heat treatment, at least the portion of the cuprate
powder manifests super conductivity at a temperature above 77K.

15 2. Method of claim 1, wherein the cuprate powder has the general
nominal formula $M_{3-m}M'_mCu_3O_{9-\delta}$, where \underline{m} is about 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 the group consisting of Ba, Ca, and Sr, and M' is
one or more elements selected from the group consisting of Y, La, Eu, Lu, and Sc.

20 3. Method of claim 2, wherein the cuprate powder is a cuprate powder of
nominal composition $Ba_2YCu_3O_{9-\delta}$.

4. Method of any claims 1-3, wherein at least the portion of the cladding
that is in contact with the powder consists essentially of normal metal that is
substantially inert with respect to oxygen and with respect to the powder under the
25 heat treating conditions.

5. Method of any of claims 1-3, wherein the cladding comprises a
diffusion barrier, with at least the portion of the diffusion barrier that is in contact
with the powder consisting essentially of normal metal that is substantially inert with
respect to oxygen and with respect to the cuprate powder under the heat treating



conditions.

6. Method of claim 5, wherein at least the portion of the diffusion barrier comprises material selected from the group consisting of Ag and Au.

5 7. Method of claim 1, wherein the cross-section-reducing operation comprises wire drawing, swaging, extrusion, or rolling.

8. Method of claim 3, wherein 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

10 ii) maintaining, during at least a part of the heat treatment, at least a portion of the cuprate powder in contact with an effective oxygen concentration such that, upon completion of the heat treatment, the oxygen content of at least the portion of the sintered cuprate powder corresponds to $\delta - 2.1$.

15 9. Method of claim 1 or 8, wherein the powder comprises oxygen donor material adapted for providing an or the effective oxygen concentration.

10. Method of claim 1 or 8, 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.

20 11. Method any of claims 1-10, further comprising a shaping operation carried out on the elongate body prior to the completion of heat treating.

12. Method of claim 11, wherein the shaping operation comprises forming a helical coil.

25 13. Method of any of claims 1-12, wherein cladding comprises a precipitation-hardenable normal metal, and wherein the method comprises a precipitation hardening step.

14. Method of any of claims 1-5 and 7-13, wherein the cladding material comprises Ag.

30 15. Method of any of claims 1-3, comprising hermetically sealing the intermediate body, whereby the oxygen-containing atmosphere in contact with the cuprate powder is caused to comprise oxygen released from the cuprate powder during the heat treatment.

16. Method of claim 1 or 8, wherein the quantity of powder comprises at least one of silver oxide powder and silver powder.



17. An article of manufacture comprising an elongate superconductive body produced according to any of the preceding claims 1-16.

18. Method of producing an elongate superconductive body substantially as hereinbefore described with reference to any of the drawings.

5 19. An elongate superconductive body substantially as hereinbefore described with reference to any of the drawings.

DATED this EIGHTH day of NOVEMBER, 1989

AMERICAN TELEPHONE and TELEGRAPH COMPANY

Patent Attorneys for the Applicants
SPRUSON & FERGUSON



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FIG. 1

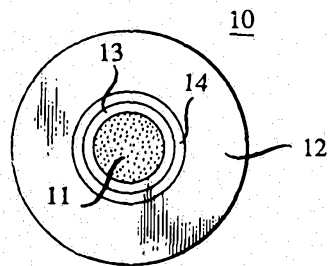


FIG. 2

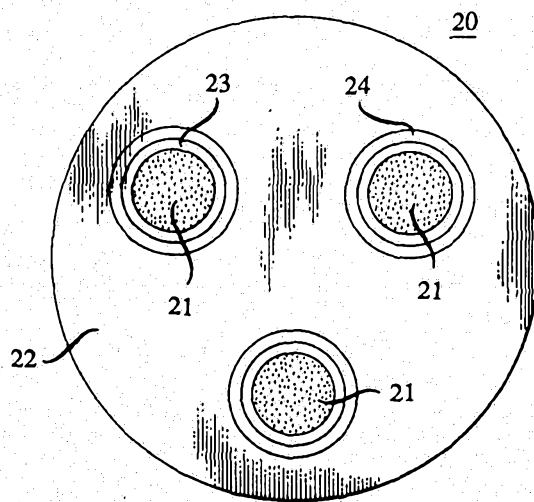


FIG. 3

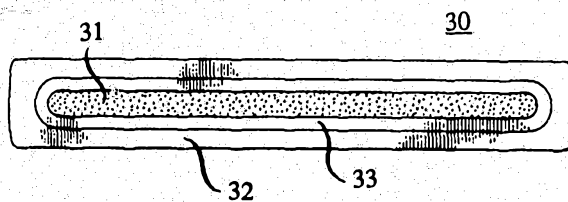


FIG. 4

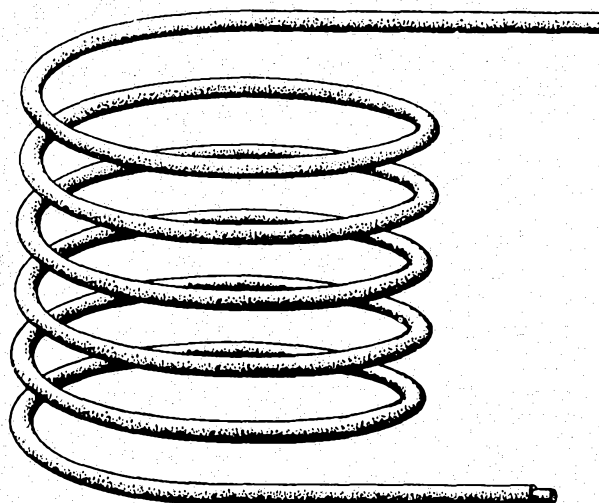


FIG. 5

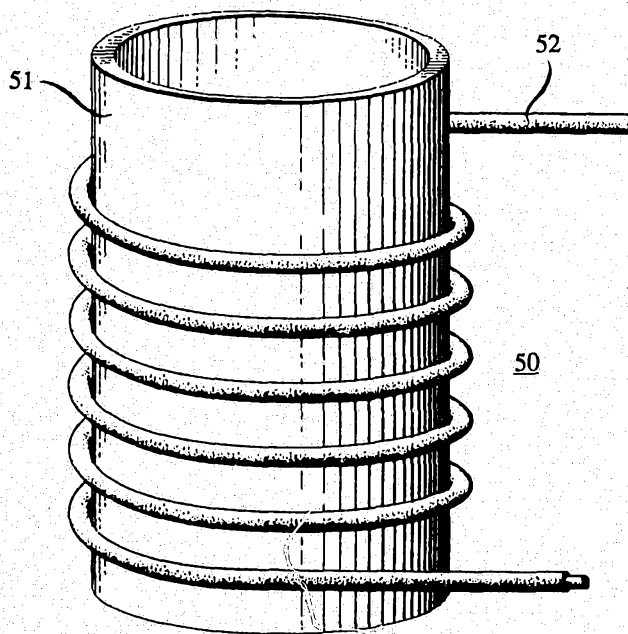


FIG. 6

