

Description

Background of the Invention

Field of the Invention

The present invention relates to a process for manufacturing a superconducting composite, more particularly it relates to a process for manufacturing an elongated superconducting composite continuously.

Description of the related art

Under the superconducting condition, the perfect diamagnetism is observed and no difference in potential is observed for all that an electric current of a constant finite value is observed internally, and hence, a variety of applications of superconductivity have been proposed in a field of electric power transmission as a mean for delivering electric power without loss.

The superconductivity can be utilized in the field of power electric applications such as MHD power generation, power transmission, electric power reservation or the like; in the field of transportation such as magnetic levitation trains or magnetically propelled ships; high sensitive sensors or detectors for sensing very weak magnetic fields, microwave, radiant ray or the like, in the medical field such as high-energy beam radiation unit; in the field of science such as NMR or high-energy physics; or in the field of fusion power generation.

In addition to the abovementioned power electric applications, the superconducting materials can be used in the field of electronics, for example, as a Josephson device which is an indispensable switching device for realizing a high-speed computer which consumes very reduced power.

However, the critical temperature could not exceed 23.2 K in Nb_3Ge which was the highest T_c heretofore for all studies for the past ten years.

Possibility of existence of a new type of superconducting materials having much higher T_c was revealed by Bednorz and Müller who discovered a new oxide type superconductor in 1986 [Z. Phys. B64 (1986) 189].

It had been known that certain ceramics material of compound oxides exhibit the property of superconductivity. For example, U. S. patent No. 3,932,315 discloses Ba-Pb-Bi type compound oxides which show superconductivity and Japanese patent laid-open No. 60-173,885 discloses that Ba-Bi type compound oxides also show superconductivity. These types of superconductors, however, possess a rather low transition temperature of about 10 K and hence usage of liquidized helium (boiling point of 4.2 K) as cryogen is indispensable to realize superconductivity.

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This new oxide type of superconducting material discovered by Bednorz and Müller is $[\text{La}, \text{Ba}]_2\text{CuO}_4$ which is called the K_2NiF_4 -type oxide having a crystal structure which is similar to known perovskite type oxide. The K_2NiF_4 -type oxides show such higher T_c as 30 K which are much higher than the known superconducting materials.

It was also reported that C. W. Chu et al discovered in the United States of America another type of superconducting material having a critical temperature in the order of 90 K in February 1987, and hence possibility of existence of high-temperature superconductors have burst on the scene.

However, the above mentioned new type of superconducting materials have been studied and developed mainly in form of sintered articles. In fact, they are produced in batch by sintering a shaped material having a predetermined dimensions in a furnace, so that no idea could be inferred therefrom for manufacturing an elongated article such as a wire continuously. Still more, the resulting sintered product is not only fragile but also difficult to be deformed.

Taking the abovementioned situation into consideration, the present inventors have proposed processes for producing sintered ceramic wires having a practically usable higher dimensional ratio of length to cross section without using organic binder which is a cause of deterioration of strength and tenacity in European patent application EP-A-0 281 444 entitled "Process for manufacturing a superconducting wire of compound oxide-type ceramic" filed February 5, 1988 and EP-A-0 281 474 titled "Process for manufacturing a compound oxide-type superconducting wire" filed February 29, 1988 in which a metal pipe filled with material powder is subjected to plastic deformation such as wire-drawing technique by means of a die and then is sintered.

These solutions are themselves satisfactory but the present inventors has continued to develop another process which can produce a ceramic wire possessing higher strength and no breakage and complete the present invention.

Therefore, an object of the present invention is to overcome the abovementioned problems of the conventional technique and to provide a novel method for manufacturing an elongated superconducting wire-like composite which has high T_c , high stability as superconductor and higher dimensional stability in continuous process.

Summary of the Invention

The present invention provides a method for manufacturing an elongated superconducting composite composed of a superconductor consisting of compound oxide and a metal sheath surrounding the superconductor, including the steps of kneading a

material powder of superconducting compound oxide with a binder, continuously shaping the resulting kneaded paste into an elongated pre-form by an extruder or by coating technique, heating the pre-form continuously to remove said binder, wrapping the pre-form with a metallic sheet, and then subjecting the pre-form wrapped with the metallic sheet to sintering operation to sinter said material powder.

Thus, the essence of the present invention resides in that a series of unit operations of Shaping-Binder removal-Sintering are carried out continuously. Namely, according to the present invention, a succession of operations from shaping to sintering can be carried out continuously, so that an elongated article such as a power cable or wire is manufactured advantageously.

Still more, the metallic sheath surrounding a superconductor functions not only as a support for resisting to mechanical stress but also as a bypass circuit in case that superconductivity is accidentally broken when it is used as a power cables.

The wrapping of the superconductor by the metallic sheet may be effected by means of a conventional pipe forming machine in which the metallic sheet is supplied continuously onto an advancing pre-form or sintered body through a die so that the latter is wrapped by the metallic sheet. Opposite side ends of the wrapped metallic sheet may be joined by means of seam welding technique.

The metallic sheet may be made of one of metals selected from a group of Cu, Ag, Au, Pt, Pd, Rh, Fe, Pb, Sn, Cd, Ti, W, Mo, Zr, Hf, Ta, Nb and alloys thereof. Copper and iron are preferable because they are cheap and are easy to be deformed and stainless steel may be used when corrosion resistance is required. Ag, Pd, Rh and other precious metals are preferable in such cases when the control of the oxygen contents is required since these precious metals can release oxygen at an elevated temperature. The kind of the metallic sheath can be selected as a function of superconductors to be produced.

The superconductor has preferably a dimension in depth of less than 1.6 mm, because it is considered that superior superconductive property is observed only in the neighbourhood of a surface portion of the superconductor. The pre-form produced from the paste composed of powder mixture and binder has preferably a thickness of less than 2 mm by taking shrinkage during the drying/heating step for removing the binder and the sintering step into account.

The superconductor which can be produced by the present invention may be in a form of a tape having a thickness of less than 2 mm and in a of a wire having a diameter of less than 2 mm. When the superconducting tape is produced, the paste composed of the powder mixture and the binder may be coated or applied on a support by means of a doctor blade. The superconducting wire is advantageously produced by

an extruder.

The binder for the paste may be a mixture of polyvinylbutylal (PVB) and dibutylphthalate (DBP) as a plasticizer dissolved in toluene, or an aqueous solution of polyvinylalcohol (PVA). The binder is removed during the coated or extruded paste is heated at a temperature of 400 °C to 700 °C.

The superconductor which can be produced by the present invention may be a compound oxide represented by the formula:



in which α stands for an element selected from Ila group of the Periodic Table, β stands for an element selected from IIIa group of the Periodic Table and γ stands for an element selected from a group comprising Ia, IIb, IIIb and VIII group of the Periodic Table, and w , x , y and z are numbers each satisfying ranges of $1 \leq w \leq 5$, $1 \leq x \leq 5$, $1 \leq y \leq 15$, $1 \leq z \leq 20$. The element α is preferably Ba and the element β is preferably at least one of Y, Ho and Dy. More specially, the superconductor is preferably Ba-Y-Cu-O system, Ba-Ho-Cu-O system or Ba-Dy-Cu-O system compound oxide which possess the quasi-perovskite type crystal structure including an orthorhombically distorted perovskite or a distorted oxygen-deficient perovskite or the like.

The abovementioned type superconductors can be prepared from a powder mixture consisting of oxides and/or carbonates containing constituent elements of said superconductor. The powder mixture may include optionally oxides and/or carbonates of at least one of elements selected from a group comprising V, Nb, Ta, Mo, W, Ti, Cr, Mn, Ga, In, Cd, Sn, Tl, Pb and Zn at a atomic ratio of 0.01 to 0.15 with respect to said element γ . The material powder is preferably pulverized into fine particles having an average particle size of less than 10 μm .

The sintering step is preferably carried out at a temperature ranging from an upper limit which is the lowest melting point of a constituent powder in the powder mixture to a lower limit which is lower by 100 °C than the upper limit. If the sintering temperature is lower than the lower limit, complete sintering reaction can not be achieved and hence the resulting product will not have practical strength. To the contrary, if the sintering temperature exceeds the upper limit of melting point, liquid phase will be produced so that the sintered body melts or decomposed, resulting in lowering the T_c .

The present invention is also applicable to the other type superconductors including a compound oxide represented by a formula:



in which Θ is Bi or Tl, Φ is Sr when Θ is Bi and is Ba when Θ is Tl, m and n are numbers each satisfying ranges of $6 \leq m \leq 10$ and $4 \leq n \leq 8$ respectively, $p = 6+m+n$, q is a number which satisfies a range of $0 < q < 1$, and r is a number which satisfies a range of -2

$\leq r \leq +2$. This system is considered to be a single phase of the following compound oxide or a mixed phase consisting mainly thereof:



in which r is a number which satisfies a range of $-2 \leq r \leq +2$.

Now, the present invention will be described with reference to attached drawing which illustrates an apparatus used for carrying out the present invention.

Brief description of the drawings

Fig. 1 is an illustrative view of an apparatus which can be used for manufacturing continuously a superconducting composite according to the present invention.

The apparatus shown in Fig. 1 includes a continuous furnace being provided with two heating means at a binder-removing zone 12 and at a sintering zone 13. An elongated pre-form 14 is produced from a paste comprising a material powder and a binder by conventional extrusion technique or coating technique such as a doctor blade coating process. The pre-form or a shaped tape or wire 14 is supplied to an inlet of the binder-removing zone 12 from a coiler 15. The elongated article 14 unwound from the coiler 15 is fed continuously to the binder-removing zone 12 in which the elongated article 14 is heated at a temperature of 400 to 700 °C to remove the binder out of the elongated article 14.

After the binder-removing zone 12, the elongated article 14 is passed to a continuous lining station 16 which is positioned at the downstream end of the binder-removing zone 12. The continuous lining station 16 is provided with a drum 18 for feeding a sheet 7 of metal or alloy to a guide 19 where the sheet 17 is wound around the elongated article 14. A seam of the wound sheet 17 is welded by means of a laser welder 20 so that the elongated article 14 is wrapped by the metal sheet 17.

The resulting composite comprising the elongated article 14 and the covering sheet or outer sheath 17 is then passed to the sintering zone 13 where the composite is heated at a temperature of 850 to 950 °C to sinter the elongated article. The longitudinal dimension or length of the sintering zone 13 and the advancing velocity of the composite can be adjusted in such manner that the sintering is performed completely.

The product 21 thus obtained may be wound about a drum 22 for stock. In this embodiment, the pre-form possesses enough flexibility and self-supporting properties, since the elongated article 14 contains the binder. The apparatus shown in Fig. 1 permit to carry out the sintering operation continuously at a higher productivity.

According to a variation of the present invention, the composite comprising the elongated article and the outer sheet can be shaped or deformed into a desired configuration such as a coil or the like due to the higher flexibility and self-supporting property, so that the sintering can be performed in the condition of the coiled configuration or in a condition that the coiled is supported on any other conductive body. The existence of the sheath of metal or alloy also increases the deflective strength.

In variation, the wire-formed or tape-formed elongated composite may be shaped or deformed into a desired configuration such as a coil or a wiring line before it is passed to the sintering zone to produce a shaped superconducting article. This deformation or shaping can be effected without any damage of the material powder since the material powder is surrounded and supported by the high-strength flexible or self-supporting metallic sheet.

Now, we will describe an example of the above-mentioned process according to the present invention in reference with a special example.

At first, powders of BaCO_3 , Y_2O_3 , and CuO each having an average particle size are mixed uniformly in such proportions that the elements Y, Ba and Cu satisfy a composition of $\text{YBa}_2\text{Cu}_3\text{O}_7$ in the final sintered body.

The powder mixture is sintered preliminarily at 900 °C for 24 hours in air to obtain a cake-like solid mass of preliminary sintered body. Then, the solid mass is pulverized by means of alumina balls in a ball mill to prepare a powder having an average particle size of 4 μm . The same procedure as the abovementioned combination of preliminary sintering and pulverization is repeated for three times.

The preliminary sintered powder thus obtained is admixed with an organic binder consisting of polyvinylbutyral (PVB) dissolved in a solvent of toluene and a plasticizer of dibutylphthalate (DBP) to prepare a paste.

Then, the resulting paste is coated on a support to prepare a sheet having a thickness of about 0.8 mm, a width of 300 mm and a length of 5 mm. After the sheet supported on the support is dried, the sheet is further heated in air at 600 °C to remove the binder.

The resulting sheet can be used directly in the abovementioned apparatus so that the sheet or pre-form is sintered finally at 960 °C for 5 hours in oxygen gas.

It is apparent from the above description that the present invention provides a process for producing an elongated superconducting article of compound oxide having higher critical temperature continuously. The metallic sheath functions not only as a support to resist mechanical stress but also functions as a by-pass circuit in case that superconductivity is accidentally broken when the article is used as a power cable.

Claims

1. Method for manufacturing an elongated superconducting composite composed of a superconductor consisting of compound oxide and a metal sheath surrounding the superconductor, including the steps of kneading a material powder of superconducting compound oxide with a binder, continuously shaping the resulting kneaded paste into an elongated pre-form by an extruder or by coating technique, heating the pre-form continuously to remove said binder, wrapping the pre-form with a metallic sheet, and then subjecting the pre-form wrapped with the metallic sheet to sintering operation to sinter said material powder.
2. Method set forth in Claim 1, characterized in that said metal sheath is fed around the pre-form after the step for removing said binder or around the sintered material powder after the step for sintering the material powder.
3. Method set forth in Claim 1 or 2, characterized in that the thickness of said superconductor is less than 1.6 mm.
4. Method set forth in any one of Claims 1 to 3, characterized in that said pre-form has a form of a tape having a thickness of less than 2 mm.
5. Method set forth in any one of Claims 1 to 3, characterized in that said pre-form has a form of a wire having a diameter of less than 2 mm.
6. Method set forth in any one of Claims 1 to 5, characterized in that said binder contain polyvinylbutyral (PVB).
7. Method set forth in Claim 6, characterized in that said binder contain further dibutylphthalate (DBP) as a plasticizer.
8. Method set forth in any one of Claims 1 to 7, characterized in that said step for removing the binder is carried out at a temperature ranging from 400 to 700 °C in air.
9. Method set forth in any one of Claims 1 to 8, characterized in that said metal sheath is made of a metallic sheet which wraps the pre-form or the sintered superconductor.
10. Method set forth in Claim 9, characterized in that side margins of said metallic sheet are welded by a laser beam.
11. Method set forth in any one of Claims 1 to 10, characterized in that said metal sheath is made of one of metals selected from a group of Cu, Ag, Au, Pt, Pd, Rh, Fe, Pb, Sn, Cd, Ti, W, Mo, Zr, Hf, Ta, Nb and alloys thereof.
12. Method set forth in Claim 11, characterized in that said material powder is a sintered powder of compound oxide obtained by the steps including sintering a powder mixture of oxides and/or carbonates containing constituent elements of said superconductor.
13. Method set forth in any one of Claims 1 to 12, characterized in that said superconductor is a sintered compound oxide represented by the formula:

$$\alpha_w \beta_x \gamma_y O_z$$
 in which α stands for an element selected from IIa group of the Periodic Table, β stands for an element selected from IIIa group of the Periodic Table and γ stands for an element selected from a group comprising Ia, IIb, IIIb and VIII group of the Periodic Table, and w, x, y and z are numbers each satisfying ranges of $1 \leq w \leq 5$, $1 \leq x \leq 5$, $1 \leq y \leq 15$, $1 \leq z \leq 20$.
14. Method set forth in Claim 13, characterized in that said material powder include further oxides and/or carbonates of at least one of elements selected from a group comprising V, Nb, Ta, Mo, W, Ti, Cr, Mn, Ga, In, Cd, Sn, Tl, Pb and Zn at a atomic ratio of 0.01 to 0.15 with respect to said element γ .
15. Method set forth in Claim 13 or 14, characterized in that said material powder has an average particle size of less than 10 μm .
16. Method set forth in any one of Claims 13 to 15, characterized in that the sintering step is carried out at a temperature ranging from an upper limit which is the lowest melting point of a constituent powder in the powder mixture to a lower limit which is lower by 100 °C than the upper limit.
17. Method set forth in any one of Claims 13 to 16, characterized in that said element α is Ba and said element β is at least one of Y, Ho and Dy.
18. Method set forth in any one of Claims 1 to 12, characterized in that said superconductor is a sintered compound oxide represented by a composition:

$$\Theta_4(\Phi_{1-q}, \text{Ca}_q)_m \text{Cu}_n \text{O}_{p+r}$$
 in which Θ is Bi or Tl, Φ is Sr when Θ is Bi and is Ba when Θ is Tl, m and n are numbers each satisfying ranges of $6 \leq m \leq 10$ and $4 \leq n \leq 8$ respectively, $p = 6+m+n$, q is a number which sat-



isfies a range of $0 < q < 1$, and r is a number which satisfies a range of $-2 \leq r \leq +2$.

Patentansprüche

1. Verfahren zur Herstellung einer langgestreckten supraleitenden Zusammensetzung, die sich aus einem aus Verbundoxid bestehenden Supraleiter und einer den Supraleiter umgebenden Metallhülle zusammensetzt und das die Schritte einschließt des Knetens eines Pulvermaterials aus supraleitendem Verbundoxid mit einem Bindemittel, des kontinuierlichen Formens der erhaltenen Knetpaste in eine langgestreckte Vorform durch einen Extruder oder durch eine Beschichtungstechnik, des kontinuierlichen Erwärms der Vorform zur Entfernung des Bindemittels, des Umhüllens der Vorform mit einer Metallhülle und des anschließenden Unterwerfens der mit der Metallhülle umhüllten Vorform eines Sinterschrittes um das Pulvermaterial zu sintern.
2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Metallhülle auf die Vorform aufgebracht wird nach dem Schritt des Entfernens des Bindemittels oder auf das gesinterte Pulvermaterial herum nach dem Sinterschritt des Pulvermaterials.
3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Dicke des Supraleiters kleiner als 1,6 mm ist.
4. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Vorform die Form eines Bandes mit einer Dicke von weniger als 2 mm aufweist.
5. Verfahren nach einem der Ansprüche 1 bis 3, dadurch gekennzeichnet, daß die Vorform die Form eines Drahtes mit einem Durchmesser von weniger als 2 mm aufweist.
6. Verfahren nach einem der Ansprüche 1 bis 5, dadurch gekennzeichnet, daß das Bindemittel Polyvinylbutyral (PVB) aufweist.
7. Verfahren nach Anspruch 6, dadurch gekennzeichnet, daß das Bindemittel außerdem Dibutylphthalat (DBP) als Plastifizierungsmittel enthält.
8. Verfahren nach einem der Ansprüche 1 bis 7, dadurch gekennzeichnet, daß der Schritt des Entfernens des Bindemittels in Luft bei einer Temperatur im Bereich von 400 bis 700° C durchgeführt wird.
9. Verfahren nach einem der Ansprüche 1 bis 8, dadurch gekennzeichnet, daß die Metallhülle aus einer metallischen Hülle besteht welche die Vorform oder den gesinterten Supraleiter umhüllt.
10. Verfahren nach Anspruch 9, dadurch gekennzeichnet, daß die Ränder der metallischen Hülle durch einen Laserstrahl verschweißt werden.
11. Verfahren nach einem der Ansprüche 1 bis 10, dadurch gekennzeichnet, daß die Metallhülle aus einem Metall besteht, das ausgewählt ist aus der Gruppe Cu, Ag, Au, Pt, Pd, Rh, Fe, Pb, Sn, Cd, Ti, W, Mo, Zr, Hf, Ta, Nb und deren Legierungen.
12. Verfahren nach Anspruch 11, dadurch gekennzeichnet, daß das Pulvermaterial ein gesintertes Pulver eines Verbundoxids ist, welches durch die Schritte erhalten wird, die das Sintern eines Pulvergemisches aus Oxiden und/oder Karbonaten einschließen, die die Bestandteile des Supraleiters aufweisen.
13. Verfahren nach einem der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß der Supraleiter ein gesintertes Verbundoxid ist, das durch die folgende Formel dargestellt wird:

$$\alpha w \beta x y y O z$$
wobei α für ein Element steht das ausgewählt ist aus der IIa-Gruppe des Periodensystems, β für ein Element steht das ausgewählt ist aus der IIIa-Gruppe des Periodensystems und γ für ein Element steht das ausgewählt ist aus der Gruppe umfassend die Ia, IIb, IIIb und VIII-Gruppen des Periodensystems und wobei w, x, y und z Zahlen sind, welche die folgenden Bereiche erfüllen $1 \leq w \leq 5, 1 \leq x \leq 5, 1 \leq y \leq 15, 1 \leq z \leq 20$.
14. Verfahren nach Anspruch 13, dadurch gekennzeichnet, daß das Pulvermaterial außerdem Oxide und/oder Karbonate umfaßt wenigstens eines der Elemente ausgewählt aus einer Gruppe umfassend V, Nb, Ta, Mo, W, Ti, Cr, Mn, Ga, In, Cd, Sn, Tl, Pb und Zn in einem Atomverhältnis von 0,01 bis 0,15 bezüglich des Elementes γ .
15. Verfahren nach Anspruch 13 oder 14, dadurch gekennzeichnet, daß das Pulvermaterial eine durchschnittliche Teilchengröße von weniger als 10 μ m aufweist.
16. Verfahren nach einem der Ansprüche 13 bis 15, dadurch gekennzeichnet, daß der Sinterschritt durchgeführt wird in einem Temperaturbereich der von einer oberen Grenze welche dem untersten Schmelzpunkt eines Pulverbestandteils im Pulvergemisch entspricht bis zu einer unteren Grenze, die um 100° C niedriger liegt als die obere



re Grenze, reicht.

17. Verfahren nach einem der Ansprüche 13 bis 16, dadurch gekennzeichnet, daß das Element α Ba ist und daß das Element β wenigstens eines der Elemente Y, Ho und Dy ist.

18. Verfahren nach einem der Ansprüche 1 bis 12, dadurch gekennzeichnet, daß der Supraleiter ein gesinteres Verbundoxid ist, das durch die folgende Formel dargestellt wird:



wobei Θ Bi oder Tl ist, Φ Sr ist, wenn Θ Bi ist und Ba ist, wenn Θ Tl ist, m und n Zahlen sind welche die Bereiche $6 \leq m \leq 10$ bzw. $4 \leq n \leq 8$ erfüllen, $p = (6+m+n)$ ist, q eine Zahl ist, welche den Bereich $0 < q < 1$ erfüllt und r eine Zahl ist, welche den Bereich $-2 \leq r \leq +2$ erfüllt.

Revendications

1. Procédé pour la fabrication d'un composite supraconducteur allongé, composé d'un supraconducteur constitué d'un oxyde composé et d'une gaine métallique entourant le supraconducteur, comprenant les étapes de malaxage d'une poudre de matériau en oxyde composé supraconducteur avec un liant, façonnage continu de la pâte malaxée résultante en une préforme allongée, au moyen d'une extrudeuse ou par une technique de revêtement, chauffage de la préforme en continu pour l'élimination dudit liant, enveloppement de la préforme avec une feuille métallique, et ensuite soumission de la préforme, enveloppée avec la feuille métallique, à une opération de frittage pour fritter ladite poudre de matériau.

2. Procédé selon la revendication 1, caractérisé en ce que ladite gaine métallique est amenée autour de la préforme après l'étape d'élimination dudit liant ou autour de la poudre de matériau frittée, après l'étape de frittage de la poudre.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que l'épaisseur dudit supraconducteur est inférieure à 1,6 mm.

4. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que ladite préforme a la forme d'une bande ayant une épaisseur de moins de 2 mm.

5. Procédé selon l'une quelconque des revendications 1 à 3, caractérisé en ce que ladite préforme a la forme d'un fil ayant un diamètre de moins de 2 mm.

6. Procédé selon l'une quelconque des revendications 1 à 5, caractérisé en ce que ledit liant contient du polyvinylbutylal (PVB).

7. Procédé selon la revendication 6, caractérisé en ce que ledit liant contient en outre du phtalate de dibutyle (DBP) en tant que plastifiant.

8. Procédé selon l'une quelconque des revendications 1 à 7, caractérisé en ce que ladite étape pour l'élimination du liant est effectuée à l'air et à une température allant de 400 à 700°C.

9. Procédé selon l'une quelconque des revendications 1 à 8, caractérisé en ce que ladite gaine métallique est faite d'une feuille métallique qui entoure la préforme ou le supraconducteur fritté.

10. Procédé selon la revendication 9, caractérisé en ce que les marges latérales de ladite feuille métallique sont soudés par un rayon laser.

11. Procédé selon l'une quelconque des revendications 1 à 10, caractérisé en ce que ladite gaine métallique est faite d'un des métaux choisis parmi Cu, Ag, Au, Pt, Pd, Rh, Fe, Pb, Sn, Cd, Ti, W, Mo, Zr, Hf, Ta, Nb et leurs alliages.

12. Procédé selon la revendication 11, caractérisé en ce que ladite poudre de matériau est une poudre frittée d'oxyde composé obtenue par les étapes comprenant le frittage d'un mélange pulvérulent d'oxydes et/ou de carbonates contenant les éléments constitutifs dudit supraconducteur.

13. Procédé selon l'une quelconque des revendications 1 à 12, caractérisé en ce que ledit supraconducteur est un oxyde composé fritté, représenté par la formule:



dans laquelle α représente un élément choisi dans le groupe IIa du tableau périodique, β représente un élément choisi dans le groupe IIIa du tableau périodique et γ représente un élément choisi dans un groupe comprenant le groupe Ia, IIb, IIIb et VIII du tableau périodique, et w, x, y et z sont des nombres rentrant chacun dans les intervalles de $1 \leq w \leq 5$, $1 \leq x \leq 5$, $1 \leq y \leq 15$, $1 \leq z \leq 20$.

14. Procédé selon la revendication 13, caractérisé en ce que ladite poudre de matériau comprend en outre des oxydes et/ou des carbonates d'au moins un des éléments choisis parmi V, Nb, Ta, Mo, W, Ti, Cr, Mn, Ga, In, Cd, Sn, Tl, Pb et Zn, en un rapport atomique de 0,01 à 0,15 par rapport audit élément γ .



15. Procédé selon la revendication 13 ou 14, caractérisé en ce que ladite poudre de matériau a une taille moyenne de particules inférieure à 10 μm .
16. Procédé selon l'une quelconque des revendications 13 à 15, caractérisé en ce que l'étape de frittage est effectuée à une température dans l'intervalle allant d'une limite supérieure qui est le plus bas point de fusion d'une poudre constitutive dans le mélange de poudres, à une limite inférieure qui est inférieure de 100°C à la limite supérieure. 5 10
17. Procédé selon l'une quelconque des revendications 13 à 16, caractérisé en ce que ledit élément α est Ba et ledit élément β est au moins l'un parmi Y, Ho et Dy. 15
18. Procédé selon l'une quelconque des revendications 1 à 12, caractérisé en ce que ledit supraconducteur est un oxyde composé fritté, représenté par la composition: 20
- $$\Theta_4(\Phi_{1-q}\text{Ca}_q)_m\text{Cu}_n\text{O}_{p+r}$$
- dans laquelle Θ est Bi ou Tl, Φ est Sr lorsque Θ est Bi et est Ba lorsque Θ est Tl, m et n sont des nombres rentrant chacun dans les intervalles de 25
- $$6 \leq m \leq 10 \text{ et } 4 \leq n \leq 8, \text{ respectivement, } p = 6 + m + n, q \text{ est un nombre rentrant dans l'intervalle de } 0 < q < 1, \text{ et } r \text{ est un nombre rentrant dans l'intervalle de } -2 \leq r \leq +2. 30$$

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