Production of magnesium diboride wires

Grivel, Jean-Claude Roger

Publication date:
2023

Document Version
Publisher's PDF, also known as Version of record

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
17 August 2023 (17.08.2023)

WIPO | PCT

(10) International Publication Number
WO 2023/152331 A1

(51) International Patent Classification:
H10N 60/20 (2023.01) *H10N 60/01* (2023.01)

(21) International Application Number:
PCT/EP2023/053376

(22) International Filing Date:
10 February 2023 (10.02.2023)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
22156613.6 14 February 2022 (14.02.2022) EP

(71) Applicant: **DANMARKS TEKNISKE UNIVERSITET** [DK/DK]; Anker Engelunds Vej 101, 2800 Kongens Lyngby (DK).

(72) Inventor: **GRIVEL, Jean-Claude Roger**; c/o Danmarks Tekniske Universitet, Anker Engelunds Vej 101, 2800 Kongens Lyngby (DK).

(74) Agent: **GUARDIAN IP CONSULTING I/S**; Diplomvej, Building 381, 2800 Kgs. Lyngby (DK).

(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:
— *of inventorship (Rule 4.17(iv))*

Published:
— *with international search report (Art. 21(3))*

(54) Title: PRODUCTION OF MAGNESIUM DIBORIDE WIRES

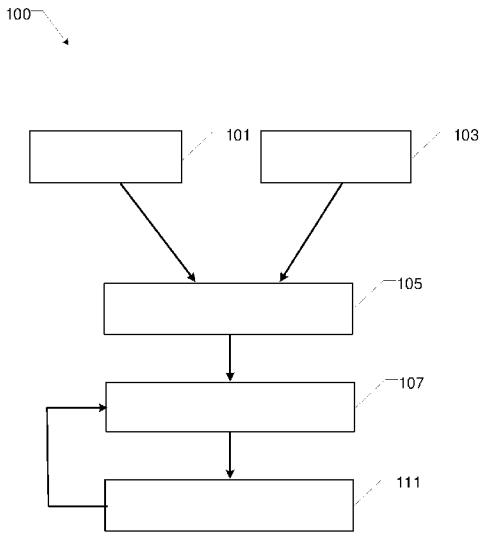

FIG. 1

(57) Abstract: The present disclosure relates to a method of manufacturing a wire comprising MgB_2 wire, where the method comprises the following steps, (a) providing a substantially tubular component having a lengthwise cavity, the tubular component being provided as a preform comprising compacted amorphous Boron powder, (b) providing a Magnesium-comprising component, (c) forming a composite billet by inserting the Magnesium-comprising component into the cavity of the tubular component, and by inserting the tubular component into an outer container such that the outer container surrounds the first tubular component, (d) performing a plastic deformation treatment of the composite billet to produce a deformed wire having a cross-section with predetermined wire cross-section dimension(s), (e) heating the deformed wire by thermal treatment to a temperature above the melting point of Mg.

WO 2023/152331 A1

PRODUCTION OF MAGNESIUM DIBORIDE WIRES

The present disclosure relates to a method of manufacturing a wire comprising MgB_2, the superconducting MgB_2 wire obtained with the method of manufacturing and use of superconductor wires based on MgB_2 wires obtained with the method of manufacturing.

BACKGROUND OF THE INVENTION

MgB_2, Magnesium diboride, is known to exhibit superconductivity whereby its electrical resistance drops to zero below a critical temperature. A superconductor is a material in which an electrical current can flow without any resistance and such materials exhibit the phenomenon of superconductivity only below a transition temperature, also called the critical temperature, denoted T_c. Magnesium diboride has a T_c= 39 K and can thus be used as a superconductor without necessitating liquid helium for cooling.

While there are superconductors with a higher critical temperature, MgB_2 is very cheap and easy to process in the form of wires in comparison with the so-called high-T_c oxides. Long superconducting wires can be utilised for a multitude of applications, for example as power cables with reduced energy losses, and in the form of superconducting windings in high-field magnets, which in turn are used in e.g. MRI scanners, induction heaters, generators, motors, magnets for particle accelerators, and fusion reactors.

Three known methods for the manufacture of wires comprising MgB_2 are: ex-situ powder-in-tube (PIT), in-situ powder-in-tube (PIT), and so-called Internal Magnesium Diffusion (IMD). In all of these methods material is introduced into an metal tube to produce a composite billet, which is then mechanically deformed and heat treated resulting in a product comprising brittle, polycrystalline, superconducting MgB_2 with the external metal sheath acting to maintain the mechanical integrity of the MgB_2.

In the ex-situ powder-in-tube (PIT) method, pre-reacted MgB_2 powder, i.e. MgB_2 powder, is loaded into a metal tube made of e.g. Fe, Ni or Cu with or without a diffusion barrier (e.g. Nb) and following this the metal tube is mechanically deformed into a wire to reach a cross-section area of about 2 mm^2 or less. Several of these wires may then be bundled, inserted into a second metallic tube and deformed again to produce a multi-filament wire. The ex-situ method requires a final sintering step at 800-950°C to ensure a sufficient connectivity between the grains of MgB_2.

The in-situ powder-in-tube (PIT) method is very similar to the ex-situ method with the fundamental difference being that a mixture of Mg and B powders is loaded into a metal tube instead of a pre-reacted MgB_2 powder. Following this, similar mechanical deformation is performed as in the ex-situ method, and MgB_2 superconductor wire is formed by reaction inside a metal sheath at 700-900°C after the mechanical deformation process.

The in-situ PIT method results in superconducting wires with a better performance than the ex-situ PIT method. Nevertheless, due to the higher density (2.57 g/cm^3) of MgB_2 compared to that of Mg (1.74 g/cm^3) and B (2.37 g/cm^3), the thermal reaction in the ex-situ method results in a larger amount of micro-pores, i.e. space between the grains, which significantly reduces the contact area between adjacent MgB_2 grains thereby limiting the achievable performance of the superconducting wire.

The "Internal Magnesium Diffusion" (IMD) method was initially developed for producing MgB_2 bulk samples, i.e. not wires, and entails melting a bulk piece of metallic Mg to the point of liquefaction, while the Mg is in contact with a compacted body of B powder. The melting point of Mg is 650°C, and therefore the temperature during thermal treatment is increased to just above the melting point of Mg, e.g. to 660°C, whereby the Mg becomes liquid, infiltrates the compacted B body, and reacts with it. This process results in a very dense MgB_2 sample.

The first attempts at applying the IMD method to the manufacture of MgB_2 wires involved packing B powders into a Mg tube, which was itself encased in an external metal tube. After mechanical deformation and reaction, a dense MgB_2 filament had formed inside the wire. Although the space initially occupied by the Mg was now empty, the wires exhibited excellent superconducting properties owing to the high ceramic density of the MgB_2 filament as described e.g. by Kulich *et al.*, Supercond. Sci. Technol. 29 (2016) 035004. A significant drawback to using this method is that there is only little contact, if any at all, with the external metal sheath and as a consequence, the superconducting filament is very easily broken during handling. Thus, this process produces a wire, which cannot be wound into a coil.

An improved IMD method later employed is disclosed in EP1361617B1. In this alternative IMD method a rod of metallic Mg is inserted into a metal tube. The rod is held in place in the middle of the tube, while B powder is filled into the cavity between the rod and the metal tube in steps with compacting of the B powder being performed using a cylindrical stamp in-between the multiple steps of filling. After mechanical deformation

and reaction the process results in a wire with a central hole in the space that was occupied by the Mg rod and a highly dense MgB_2 layer in contact with the internal wall of the metal tube. Thus, the improved IMD method has produced a wire comprising MgB2, which does not have the drawback of being brittle. However, the method has its own drawbacks such as the manufacturing technique being complicated by the packing of the B powder.

There is thus a need for an less complicated and more reproducible method of manufacturing high-performance MgB_2 wires.

It is an object to provide an improved method of manufacturing wires comprising MgB_2.

It is a further object in some embodiments to provide a method of manufacturing that mitigates or solves at least some of the above or other drawbacks.

SUMMARY OF THE INVENTION

In a first aspect is provided a method of manufacturing a wire comprising MgB_2, in a second aspect is provided a superconducting MgB_2 wire obtained with the method according to the first aspect, and in a third aspect is disclosed use of superconductor wires based on MgB_2 wires obtained with the method according to the first aspect to form superconductor end products. In the aspects, the terms and features relate to the terms and features having the same name in other aspects and therefore the descriptions and explanations of terms and features given in one aspect apply to the other aspects.

In the first aspect, a method of manufacturing a wire comprising MgB_2 wire is disclosed. The method comprises the steps:

- providing a substantially tubular component having a lengthwise cavity, where the tubular component is provided as a preform comprising compacted amorphous Boron powder,
- providing a Magnesium-comprising component,
- forming a composite billet by inserting the Magnesium-comprising component into the cavity of the tubular component, and by inserting the tubular component into a substantially tubular outer container such that the outer container surrounds the first tubular component,

- performing one or more plastic deformation treatments (107) and one or more thermal treatments (111) on the composite billet to produce a wire comprising MgB_2.

Thus, the B powder is primed as a firm preform, which makes the formation of the composite billet far easier and less complex than previously employed methods. A production method that is facilitated by the method of manufacturing disclosed herein will therefore result in a lower cost overall making the wires comprising MgB_2 cheaper to produce. Further, the distribution of B grains can be made more homogenous, which in turn leads to an improved MgB_2 microstructure after thermal treatment and thereby an increased performance of the superconducting wire.

The method steps may be performed in any order that makes technical sense and some may be performed simultaneously. Particularly, providing the tubular component and providing the Mg-comprising component may be done in any order or simultaneously. Further, when forming the composite billet, whereby the tubular component is inserted in an outer container this may be done before or after the Mg-comprising component has been inserted into the cavity of the tubular component.

The cross-section of the outer surface of the tubular component may be an ellipse or a polygon, e.g. the cross-section may be circular, oval, square, triangular, etc. Thus, in some embodiments, the cross-section of the outer surface of the tubular component is substantially elliptical or polygonal. Likewise, the cross-section of the inner surface of the tubular component, i.e. the surface of the cavity may be an ellipse or a polygon, e.g. the cross-section may be circular, oval, square, triangular, etc. Thus, in some embodiments, the cross-section of the cavity is substantially elliptical or polygonal. The surface of the cavity may be a shape that is similar to that of the outer surface of the tubular component, or the surface of the cavity may be a shape that is different to that of the outer surface of the tubular component. For example, the cross-section of both the inner and outer surface of the tubular component may be circular, or the cross-section of the outer surface of the tubular component may be round, while the cross-section of the inner surface may be square. Thus, in some embodiments, the cross-section shape of the outer surface of the tubular component and the cross-section of the cavity are the same shape, or the cross-section of the outer surface of the tubular component and the cross-section of the cavity are different shapes.

The cavity may extend along the lengthwise axis, i.e. centrally in the tubular component, or be shifted compared to the lengthwise axis of the tubular component.

In some embodiments, the method steps of providing a substantially tubular component and of providing a Magnesium-comprising component further comprises configuring the two components such that the weight ratio of Magnesium to Boron in the composite billet is higher than 1.2.

In some embodiments, the atomic ratio of Magnesium/Boron in the composite billet is substantially equal to 0.5, i.e. the composition is aimed at having a stoichiometric ratio. However, it may be advantageous to use a non-stoichiometric ratio of Mg/B as this may affect the reaction between Mg and B, such as affect the reaction rate of the formation of MgB_2. Further, a non-stoichiometric ratio of Mg/B in the composite billet may affect the homogeneity of the final product, i.e. of the wire comprising MgB_2. A non-stoichiometric ratio of Mg/B in the composite billet may lead to impurities in the final product, such as e.g. Mg, MgB_4, MgB_7 impurities. Altering the characteristics of the wire comprising MgB_2 may result in a superconducting product, which exhibits more flux pinning. Thus, in some embodiments the atomic ratio of Magnesium/Boron in the composite billet is different from 0.5.

In some embodiments, the Mg-comprising component is shaped as a rod, i.e. as a solid bar. In some embodiments, the cross-section of the Mg-comprising component is an ellipse or a polygon. In some embodiments, the cross-section of the Mg-comprising component and the cross-section of the cavity are the same shape, or the cross-section of the Mg-comprising component and the cross-section of the cavity are different shapes. Preferably, the shape of the Mg-comprising component will be configured so as to fit snugly within the cavity of the B preform. An advantage of this is easier handling of the composite billet.

In some embodiments, the Mg-comprising component comprises metallic magnesium. In some embodiments, the Mg-comprising component comprises a Mg-based alloy.

In some embodiments, the step of performing a plastic deformation treatment of the composite billet comprises deforming the composite billet using one or more of: extrusion, drawing, swaging, pressing, and/or rolling. More than one plastic deformation may be performed, or the same kind of plastic deformation may be performed more than once. A plurality of plastic deformations may be performed followed by one or more thermal treatments. During a thermal treatment the material is heated to a temperature above room temperature. One or more thermal treatment may be performed before the first plastic deformation. One or more thermal treatments may be performed in-between one or more plastic deformation treatments. Thus, in some

embodiments, the method step of performing one or more plastic deformation treatments and one or more thermal treatments comprises a plurality of plastic deformation treatments being performed, and one or more thermal treatments are applied between some or all of the successively performed plastic deformation treatments. In some embodiments, the method step of performing one or more plastic deformation treatments (107) and one or more thermal treatments comprises one or more thermal treatments being applied during one or more of the one or more plastic deformation treatments. Thermal treatments performed during one or more plastic deformation treatments may be performed at the same time as, or at least some of the time where a plastic deformation is performed.

In some embodiments, the method step of performing one or more plastic deformation treatments and one or more thermal treatments further comprises a deformed wire being produced as a result of one or more of the one or more plastic deformations. In some embodiments, the method step of performing one or more plastic deformation treatments and one or more thermal treatments further comprises cutting the deformed wire to obtain a plurality of deformed wires and assembling the plurality of deformed wires into a multi-wire construction of deformed wires. Further plastic deformation treatments and/or further thermal treatments may be performed on the plurality of deformed wires prior to, during or following their assembly in a multi-wire construction. The plurality of deformed wires may be assembled in the multi-wire construction in a hexagonal assembly.

In some embodiments, the method step of performing one or more plastic deformation treatments and one or more thermal treatments further comprises winding the deformed wire, or multi-wire construction of deformed wires, onto a support. Further plastic deformation treatments and/or further thermal treatments may be performed on the wound deformed wire or multi-wire construction prior to, during or following the winding onto a support.

Performing plastic deformation and thermal treatment at the same time may have the effect that MgB_2 is formed during the plastic deformation treatment. Thus, in some embodiments, MgB_2 is formed during the one or more plastic deformation treatments by performing one or more of the plastic deformations at a temperature higher than room temperature, preferably at a temperature above 300°C, more preferably at a temperature above 500°C. For example, MgB_2 may be formed by hot rolling, i.e. deforming the composite billet by rolling, while heating the composite billet during some

or all of the rolling process. Thus, in some embodiments, the step of performing plastic deformation and thermal treatment on the composite billet to produce a wire comprising MgB_2 comprises hot rolling.

In some embodiments, the cross-section of the outer surface of the deformed wire may be an ellipse or a polygon.

In some embodiments, the method step of providing a substantially tubular component further comprises providing the Boron-comprising preform using extrusion. In some embodiments, a C-comprising (Carbon-comprising) binder is used during the extrusion of the tubular component. An advantage of this is that it will result in C-doping of the B preform, which will in turn result in C-doping of the MgB_2 wire. It is known that C-doped MgB_2 has a higher performance compared to pure MgB_2.

The outer container will preferably be made of a material, which can sustain the temperatures of the thermal treatment without breaking down or melting and without reacting extensively with the Boron or Magnesium, or sintered products thereof. In some embodiments, the outer container is comprised of an elemental metal such as Cu, or of an alloy such as steel, a Cu/Ni alloy, and Fe alloy, or of a composite material, such as a metal-ceramic composite, such as Al/Al_2O_3. In some embodiments, the outer container comprises a plurality of metal sheaths.

In some embodiments, the outer container comprises a diffusion barrier. In some embodiments, the addition of a diffusion barrier to the outer container comprises inserting a diffusion barrier sheath into the outer container, or providing a diffusion barrier coating to the inner surface of the outer container. In some embodiments, the diffusion barrier comprises Niobium and/or Titanium.

By heating the Mg-comprising component to a temperature above the melting point of Mg, the Mg in the Mg-comprising component may liquefy and react with the B in the preform to form a wire comprising MgB_2. However, MgB_2 may also be formed by applying a temperature lower than the melting point of Mg in which case the process of forming MgB_2 usually takes longer the lower the temperature. The formation of MgB_2 may be facilitated by performing one or more plastic deformation treatments at the same time as exposing the materials to an elevated temperature. In some embodiments, the method step of performing one or more thermal treatments comprises subjecting the heated material(s) to a maximum temperature of 1050°C, preferably to a temperature of between 300°C and 950°C, more preferably to a temperature of between 500°C and 850°C. In some embodiments, performing one or

more thermal treatments comprises heating in a reducing atmosphere and/or under pressure.

For some uses of the wires comprising MgB_2 made using the method disclosed herein it may be advantageous to make a multifilament wire as is known in the art.

In the second aspect, a superconducting MgB_2 wire obtained with the method according to the first aspect is disclosed.

In some embodiments, the superconducting MgB2 wire has a length that is > 100 m.

In the third aspect, use of superconductor wires based on MgB2 wires obtained with the method according to the first aspect to form superconductor end products is disclosed.

BRIEF DESCRIPTION OF THE DRAWINGS

In the following, exemplary embodiments of the invention are described in more detail with reference to the appended drawings, wherein:

FIG. 1 shows a flow diagram illustrating steps of the method of manufacturing a wire comprising MgB_2 according to some embodiments,

FIG. 2 shows a flow diagram illustrating steps of the method of manufacturing a wire comprising MgB_2 according to some embodiments,

FIG. 3 shows a flow diagram illustrating steps of the method of manufacturing a wire comprising MgB_2 according to some embodiments,

FIGS. 4A-D illustrate method steps to form a composite billet used in the manufacture of a wire comprising MgB_2 according to some embodiments, and

FIG. 5 shows the superconducting transition measured by means of ac-susceptibility on a piece of wire manufactured according to some embodiments.

DETAILED DESCRIPTION

In the following various exemplary embodiments of the disclosed method of manufacturing a MgB_2 wire are described with reference to the appended drawings. The skilled person will understand that the accompanying drawings are schematic and simplified for clarity and therefore merely show details which are essential to the

understanding of the invention, while other details have been left out. The elements shown in the drawings are not necessarily drawn to scale, but may primarily be illustrative of relative position, orientation, and function. Like reference numerals refer to like elements throughout. Like elements will therefore not necessarily be described in detail with respect to each figure.

FIG. 1 shows a flow diagram illustrating steps of the method 100 of manufacturing a wire comprising MgB_2 according to some embodiments.

In step 101, a substantially tubular component 1 is provided by extrusion to produce a hollow preform that comprises compacted amorphous Boron powder.

For the extrusion, the boron powder can be treated with a surfactant to avoid agglomeration before mixing it with a plasticiser. The mixture is heated to a temperature of about 100°C and extruded under pressure through dies with a desired geometry. The resulting substantially tubular component is cooled down to room temperature to solidify. The plasticiser and other unwanted additives can be removed by heating the substantially tubular component to a temperature between 150°C and 500°C. This produces a stable B-comprising preform 1 that is robust and can be handled without falling apart, i.e. it maintains its shape and form. The preform 1 is tubular such that it has a central hole 3, or cavity, that extends lengthwise in the preform, see fig. 3.

In some instances, the B-comprising preform may be made to have more than one cavity. The plurality of cavities can be distributed in a regular or irregular way in the preform.

In step 103, a Mg-comprising rod 5, e.g. of metallic Magnesium, that can later be inserted into the cavity 3 of the Boron preform 1 is provided. Thus, in the preparation steps 101 and 103 the shapes of the cavity 3 in the B preform 1 and the outer dimensions of the Mg rod 5 are made to allow for the forming of a composite billet 9.

In step 105, a composite billet 9 is formed by inserting the Mg-comprising rod into the cavity 3 of the extruded preform 1, and by inserting the preform 1 into a tubular container 7. Inserting the rod and tubular objects into each other can be done in any order that is practical. The final product is the composite billet 9, where the Mg-comprising rod 5 is surrounded by the B preform 1, which is in turn surrounded by the container 7.

If the B-comprising preform has more than one cavity, a Mg-comprising rod may be inserted in one or more of the cavities. In this case, the final product may be a composite billet 9 wherein a plurality of Mg-comprising rods 5 are each surrounded by the B preform 1, and an outer container 7 surrounds the B preform.

Following the creation of the composite billet, one or more plastic deformation treatments 107 and one or more thermal treatments 111 are performed on the composite billet to produce, as a final product, a wire comprising MgB2.

An example of a method step to perform a plastic deformation and a thermal treatment on the composite billet is shown in fig. 1, wherein the composite billet is first deformed 107 and then heated 111. In step 107, a plastic deformation treatment of the composite billet 9 is made so as to produce a deformed wire with a cross-section of a predetermined dimension, for example a substantially circular cross-section with a predetermined diameter.

In step 111, the deformed wire undergoes a thermal treatment and is heated. During the thermal treatment the Mg in the rod 5 in the composite billet 9 reacts with the B in the preform 1 surrounding the rod 5.

The processing may be repeated such that the deformed wire undergoes another plastic deformation treatment 107 and/or another thermal treatment 111.

Finally, as the end product, the method produces a wire comprising MgB_2.

FIG. 2 shows a flow diagram illustrating steps of the method of manufacturing a wire comprising MgB_2 according to some embodiments.

Method steps 101, 103, 105, 107, and 111 may be as described for the embodiment in fig. 1.

After the plastic deformation in step 107 and before thermal treatment in step 111, the embodiment comprises a method step 108, wherein the deformed wire is cut so as to obtain a plurality of deformed wires, i.e. the produced deformed wire is cut into smaller pieces. The thereby obtained plurality of deformed wires are then assembled into a multi-wire construction, which is wound onto a support 109 and heated 111 to produce a multifilament wire comprising MgB_2.

FIG. 3 shows a flow diagram illustrating steps of the method of manufacturing a wire comprising MgB_2 according to some embodiments.

Method steps leading to the formation of the composite billet may be as described for the embodiment in fig. 1.

Following the creation of the composite billet in step 105, one or more plastic deformation treatments 107 and one or more thermal treatments 111 are performed on the composite billet to produce, as a final product, a wire comprising MgB2.

The plastic deformation and thermal treatments may take place in separate steps or may be done in a single process, whereby the composite billet is deformed and heated at the same time. For example, the combined deformation and heating may be in the form of hot rolling.

FIGS. 4A-D illustrate method steps to form a composite billet used in the manufacture of a wire comprising MgB_2 according to some embodiments.

In fig. 4A is illustrated a B-comprising preform 1 made by extrusion into a cylindrical tube with a central cavity 3 that extends through the preform 1. The preform 1 is shown viewed from an end in fig. 4B, where the cavity 3 can be seen to also be cylindrical in shape. In fig. 4C is shown a rod 5 of metallic Mg being inserted into the cavity 3 of the preform 1. The combined preform 1 and rod 5 is then inserted into a metal sheath 7 to form a composite billet 9 shown in fig. 4D.

FIG. 5 shows the superconducting transition measured by means of ac-susceptibility on a piece of wire manufactured according to some embodiments of the method disclosed herein. A boron tube with an external diameter of 10 mm and internal diameter of 5 mm was extruded and heated to 350°C. The tube was inserted in a Nb tube and an external Cu tube. A pure Mg rod was placed inside the boron tube to form a composite billet. After sealing the ends, the composite billet was deformed by means of groove rolling to a wire with 1.8 mm diameter. After heat treatment at 650°C, a superconducting wire was produced. Subsequent ac-susceptibility measurements on the produced wire shows that the superconducting transition takes place with an onset at 36.5 K, indicating that some carbon originating from the plasticiser used for extrusion was efficiently doped in the MgB_2 structure. The width of the superconducting transition indicates that the C-doping level is not homogeneous in this particular sample.

LIST OF REFERENCES

1	Tubular component
3	Cavity
5	Magnesium-comprising component
7	Outer container
9	Composite billet
100	method of manufacturing a MgB_2 wire
101	providing a substantially tubular component
103	providing a Magnesium-comprising component
105	forming a composite billet
107	performing one or more plastic deformation treatments
108	cutting
109	winding
111	performing one or more thermal treatments

CLAIMS

1. **A method (100) of manufacturing** a wire comprising MgB_2, the method comprising the steps:

- providing (101) a substantially tubular component (1) comprising a lengthwise cavity (3), the tubular component (1) being provided as a preform comprising compacted amorphous Boron powder,
- providing (103) a Magnesium-comprising component (5),
- forming (105) a composite billet (9) by inserting the Magnesium-comprising component (5) into the cavity (3) of the tubular component (1), and by inserting the tubular component (1) into a substantially tubular outer container (7) such that the outer container (7) surrounds the first tubular component (1),
- performing one or more plastic deformation treatments (107) and one or more thermal treatments (111) on the composite billet to produce a wire comprising MgB_2.

2. A method of manufacturing a wire comprising MgB_2 according to claim 1, wherein the method step of providing (101) a substantially tubular component (1) further comprises providing the Boron-comprising preform using extrusion.

3. A method of manufacturing a wire comprising MgB_2 according to any of the previous claims, wherein the Mg-comprising component (5) is shaped as a rod.

4. A method of manufacturing a wire comprising MgB_2 according to any of the previous claims, wherein the method step of performing one or more plastic deformation treatments (107) and one or more thermal treatments (111) further comprises a deformed wire being produced as a result of one or more of the one or more plastic deformations.

5. A method of manufacturing a wire comprising MgB_2 according to claim 4, wherein the method step of performing one or more plastic deformation treatments (107) and one or more thermal treatments (111) further comprises cutting (108) the

deformed wire to obtain a plurality of deformed wires and assembling the plurality of deformed wires into a multi-wire construction of deformed wires.

6. A method of manufacturing a wire comprising MgB_2 according to any of claims 4 or 5, wherein the method step of performing one or more plastic deformation treatments (107) and one or more thermal treatments (111) further comprises winding (109) the deformed wire, or multi-wire construction of deformed wires, when dependent on claim 5, onto a support.

7. A method of manufacturing a wire comprising MgB_2 according to any of the previous claims, wherein the method step of performing one or more plastic deformation treatments (107) and one or more thermal treatments (111) comprises a plurality of plastic deformation treatments being performed, and

wherein one or more thermal treatments are applied between some or all of the successively performed plastic deformation treatments.

8. A method of manufacturing a wire comprising MgB_2 according to any of the previous claims, wherein the method step of performing one or more plastic deformation treatments (107) and one or more thermal treatments (111) comprises one or more thermal treatments being applied during one or more of the one or more plastic deformation treatments.

9. A method of manufacturing a wire comprising MgB_2 according to any of the previous claims, wherein MgB_2 is formed during the one or more plastic deformation treatments by performing one or more of the plastic deformations at a temperature higher than room temperature, preferably at a temperature above 300°C, more preferably at a temperature above 500°C.

10. A method of manufacturing a wire comprising MgB_2 according to any of the previous claims, wherein the method step of performing one or more thermal treatments (111) comprises heating in a reducing atmosphere and/or under pressure.

11. A method of manufacturing a wire comprising MgB_2 according to any of the previous claims, wherein the method step of performing one or more thermal treatments (111) comprises heating to a maximum temperature of 1050°C, preferably to a temperature between 300°C and 950°C, more preferably to a temperature between 500°C and 850°C.

12. A method of manufacturing a wire comprising MgB_2 according to any of the previous claims, wherein the method steps of providing (101) a substantially tubular component (1) and of providing (103) a Magnesium-comprising component (5) further comprises configuring the two components (1, 5) such that the weight ratio of Magnesium to Boron in the composite billet (9) is higher than 1.2.

13. A method of manufacturing a wire comprising MgB_2 according to any of the previous claims, wherein the step of performing one or more plastic deformation treatments (107) comprises deforming the composite billet (9) using one or more of: extrusion, drawing, swaging, pressing, and/or rolling.

14. **A superconducting MgB_2 wire** obtained with the method according to any of the previous claims.

15. **Use of superconductor wires based on MgB_2 wires** obtained with the method according to any of claims 1 - 13 to form superconductor end products.

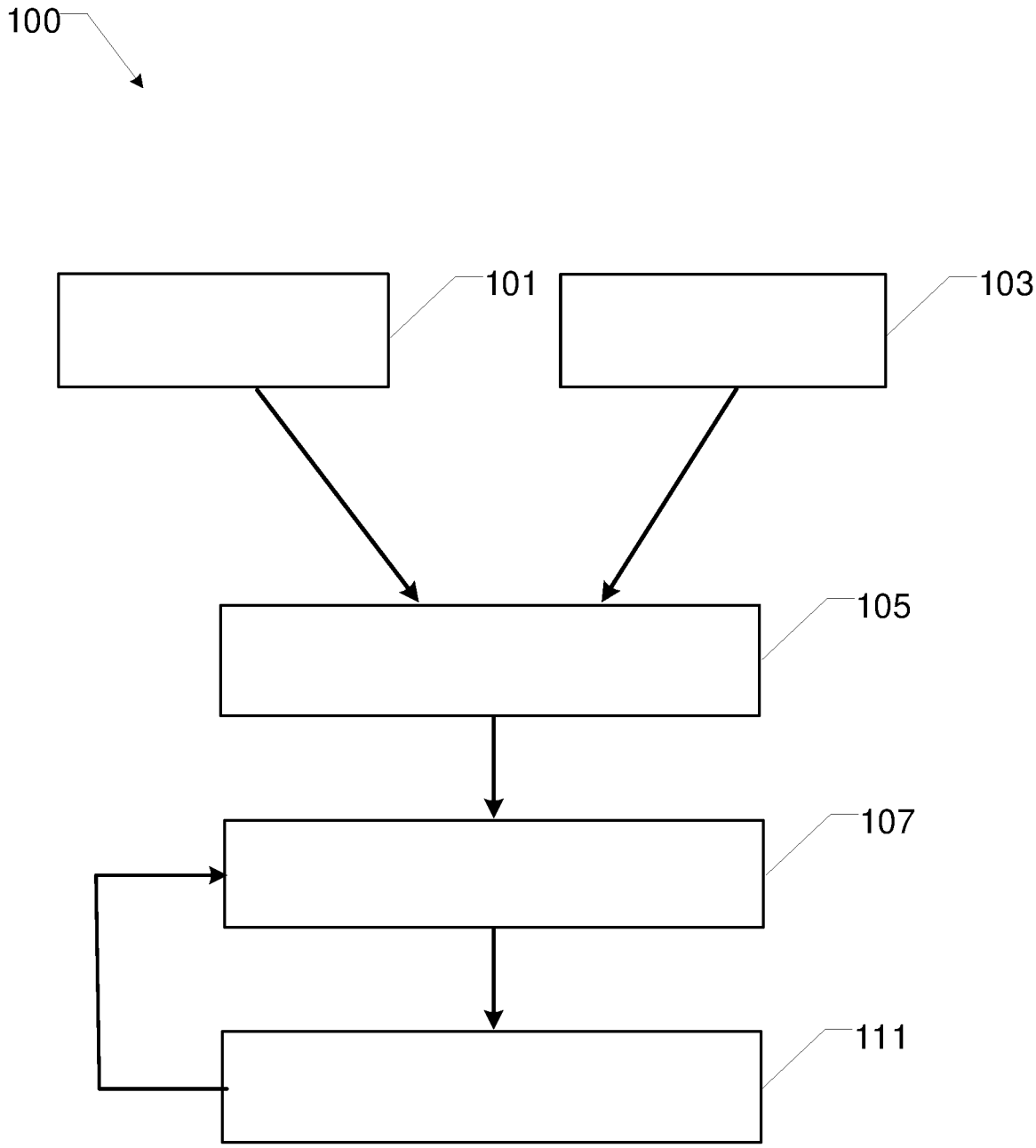

FIG. 1

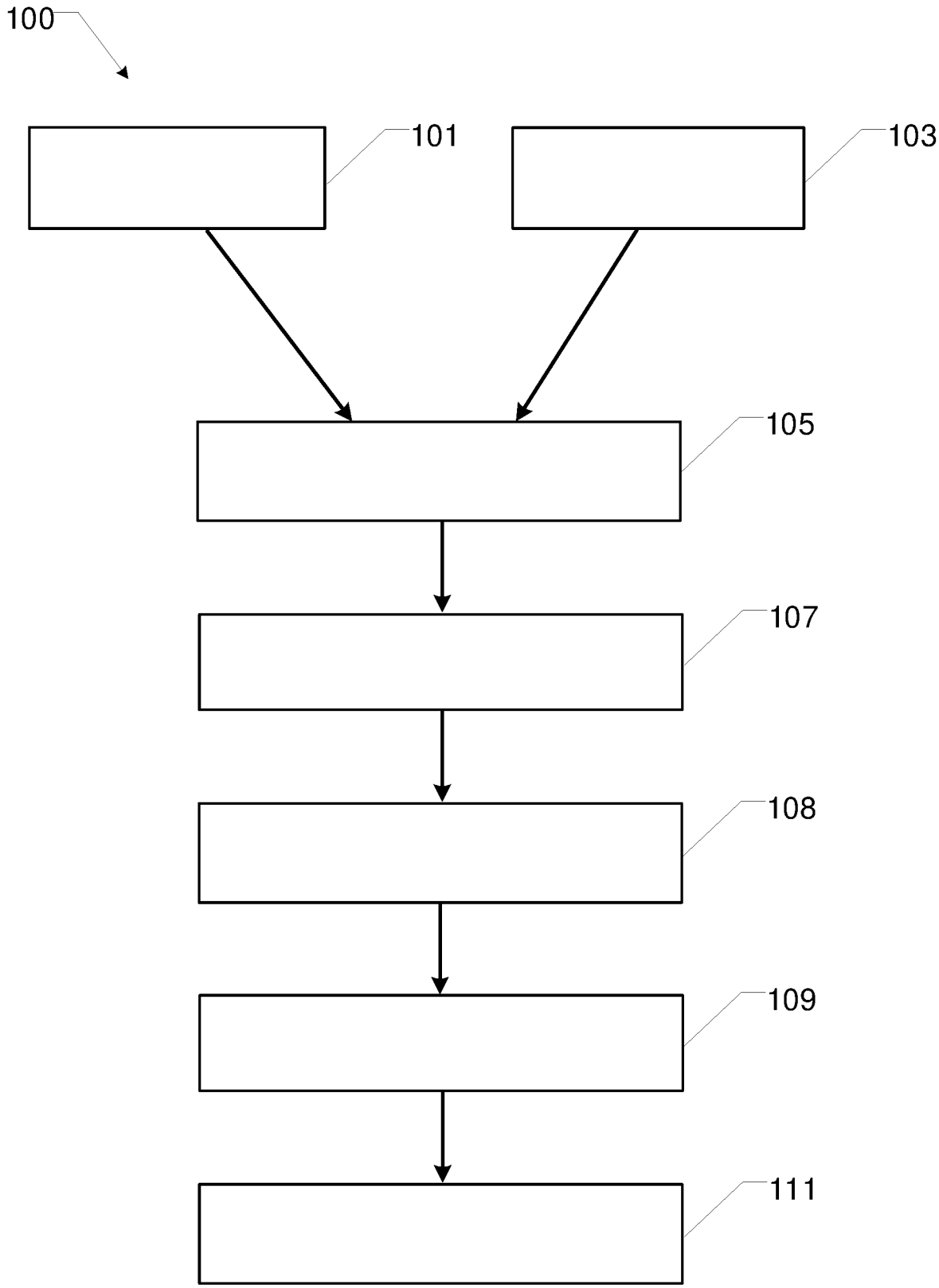

FIG. 2

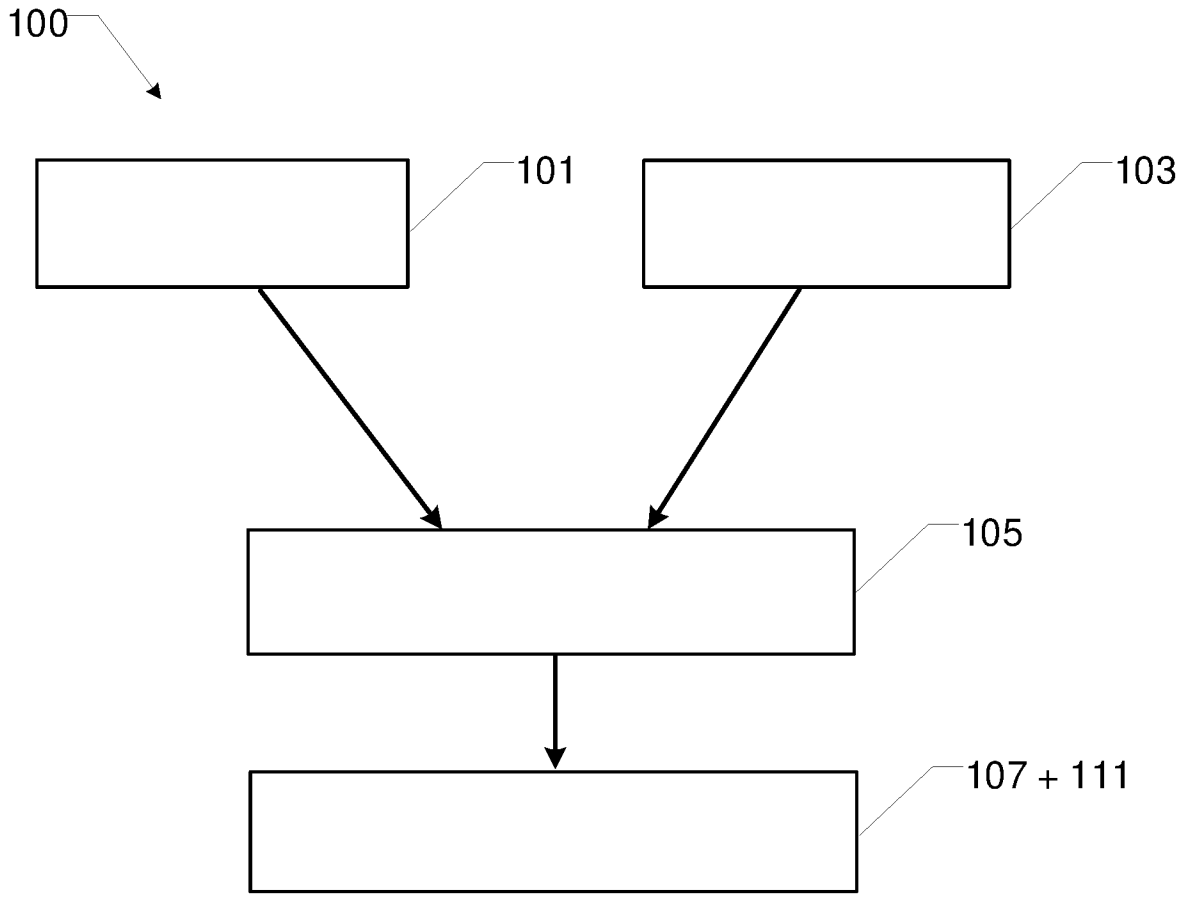

FIG. 3

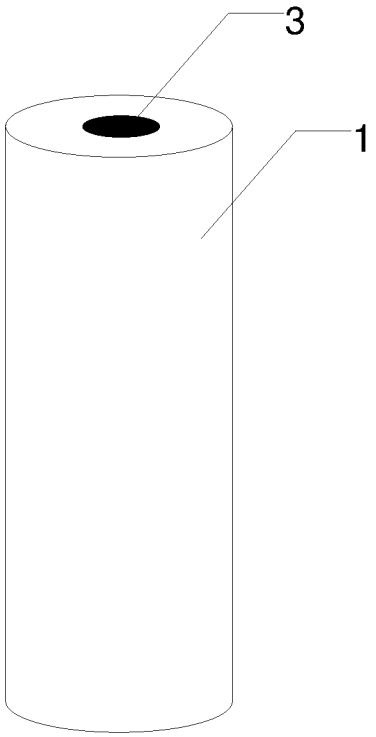

FIG. 4A

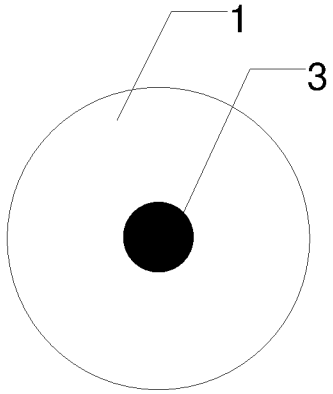

FIG. 4B

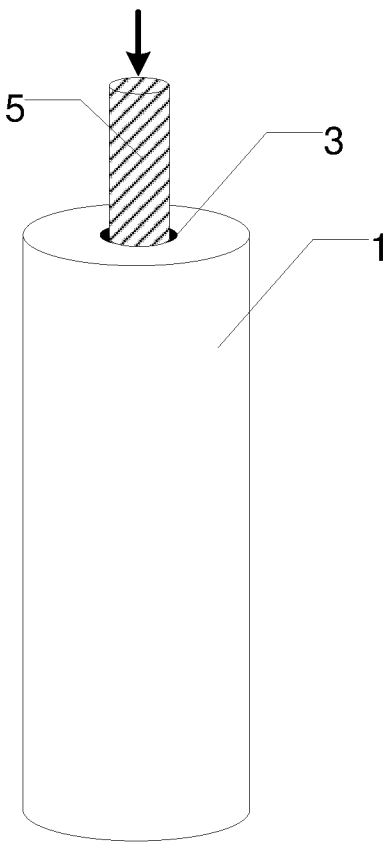

FIG. 4C

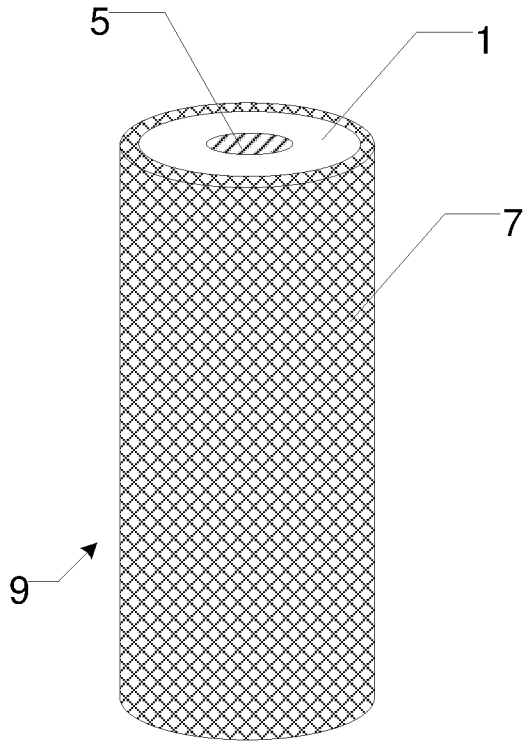

FIG. 4D

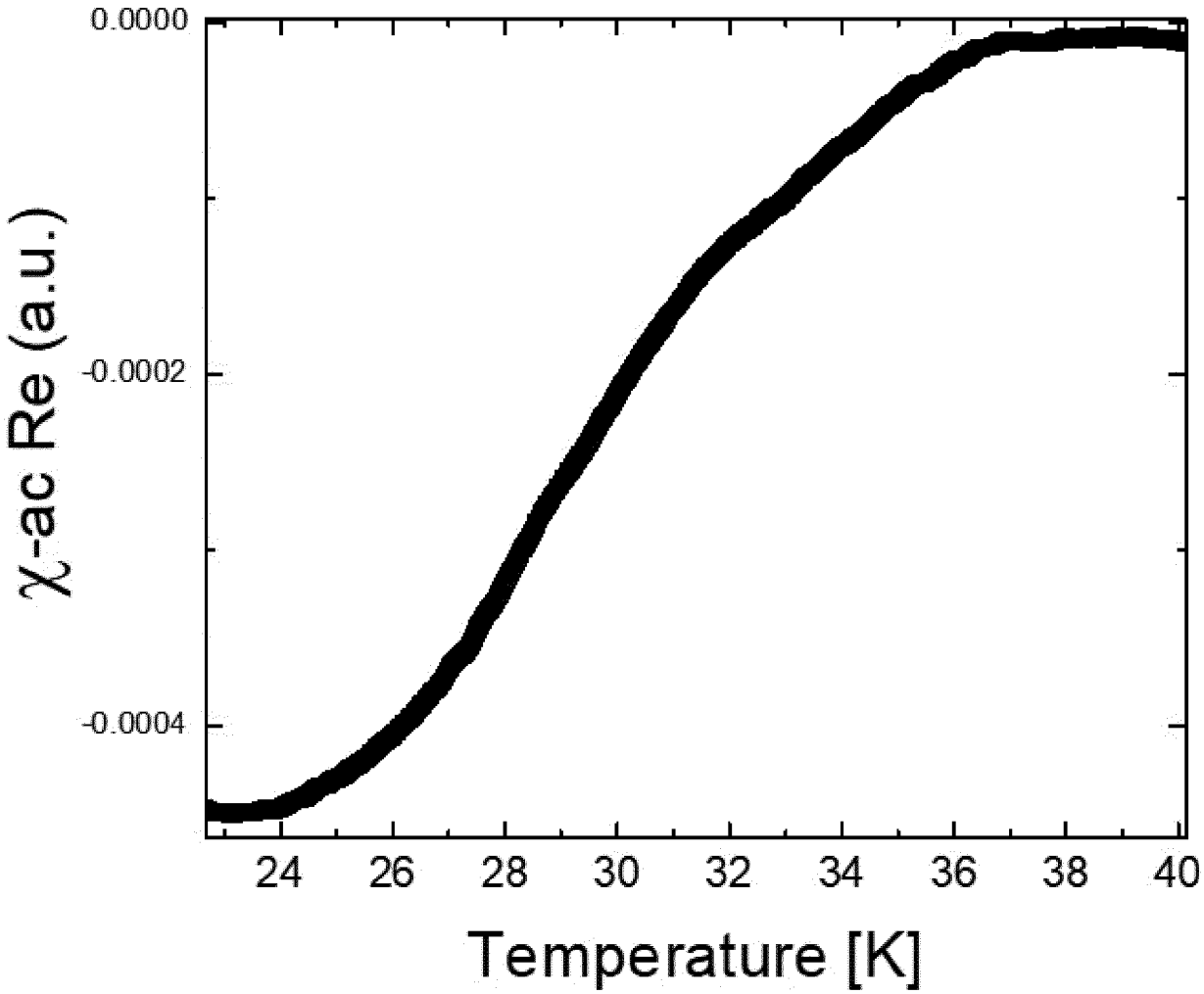
0.0000
-0.0002
-0.0004
χ-ac Re (a.u.)
24
26
28
30
32
34
36
38
40
Temperature [K]

FIG. 5

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/053376

A. CLASSIFICATION OF SUBJECT MATTER
INV. H10N60/20 H10N60/01
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HUR J M ET AL: "Fabrication of high-performance MgB2 wires by an internal Mg diffusion process", SUPERCONDUCTOR SCIENCE AND TECHNOLOGY, vol. 21, 1 January 2008 (2008-01-01), page 032001, XP093037097, DOI: 10.1088/0953-2048/21/3/032001 Retrieved from the Internet: URL:https://iopscience.iop.org/article/10.1088/0953-2048/21/3/032001/pdf>	14,15
A	figure 1	1-13

X	EP 1 361 617 B1 (EDISON SPA [IT]) 5 March 2008 (2008-03-05) cited in the application	14,15
A	paragraph [0012]	1-13

	-/--	

[X] Further documents are listed in the continuation of Box C.

[X] See patent family annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance;; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance;; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
19 April 2023	26/04/2023

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Koskinen, Timo

3

Form PCT/ISA/210 (second sheet) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No
PCT/EP2023/053376

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2008/274901 A1 (GLOWACKI BARTEK A [GB] ET AL) 6 November 2008 (2008-11-06)	14,15
A	paragraph [0081] - paragraph [0083]	1-13
A	US 2004/116301 A1 (TALLON JEFFERY [NZ] ET AL) 17 June 2004 (2004-06-17)	1-15
A	US 2016/293296 A1 (ICHIKI YOUTA [JP] ET AL) 6 October 2016 (2016-10-06)	1-15

3

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/EP2023/053376

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 1361617 B1	05-03-2008	AT 388491 T	15-03-2008
		DE 60319458 T2	12-03-2009
		DK 1361617 T3	23-06-2008
		EP 1361617 A2	12-11-2003
		ES 2303577 T3	16-08-2008
		HK 1062224 A1	21-10-2004
		IT MI20021004 A1	10-11-2003
		JP 4443855 B2	31-03-2010
		JP 2004047441 A	12-02-2004
		PT 1361617 E	17-06-2008
		SI 1361617 T1	31-08-2008
		US 2004009879 A1	15-01-2004
		US 2005159318 A1	21-07-2005
US 2008274901 A1	06-11-2008	US 2008274901 A1	06-11-2008
		WO 2008122802 A1	16-10-2008
US 2004116301 A1	17-06-2004	US 2004116301 A1	17-06-2004
		WO 02069353 A1	06-09-2002
US 2016293296 A1	06-10-2016	EP 3113192 A1	04-01-2017
		JP 6105088 B2	29-03-2017
		JP WO2015087387 A1	16-03-2017
		US 2016293296 A1	06-10-2016
		WO 2015087387 A1	18-06-2015