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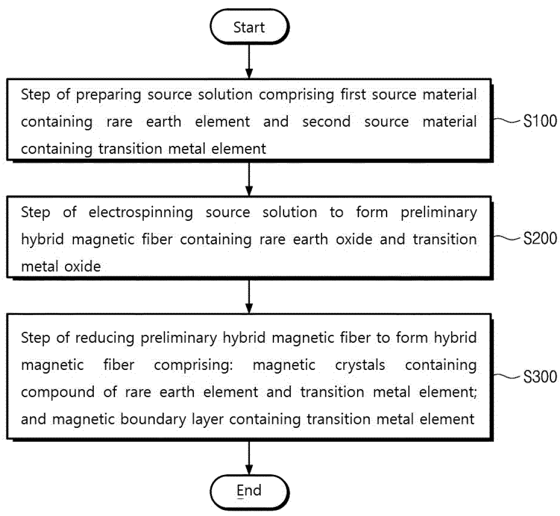
(54) **HYBRID MAGNETIC FIBER AND MANUFACTURING METHOD THEREFOR**

(57) A manufacturing method for a hybrid magnetic fiber is provided. The manufacturing method for a hybrid magnetic fiber may comprise the steps of: preparing a source solution comprising a first source material containing a rare-earth element and a second source material containing a transition-metal element; electrospinning the source solution to form a preliminary hybrid magnetic fiber containing a rare-earth oxide and a transition-metal oxide; and reducing the preliminary hybrid magnetic fiber to form a hybrid magnetic fiber, the hybrid magnetic fiber comprising: magnetic crystals containing a compound of the rare-earth element and the transition-metal element; and a magnetic boundary layer containing the transition-metal element.

【Fig. 1】



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Description

[Technical Field]

[0001] The present invention relates to a hybrid magnetic fiber and a method for preparing the same, and more specifically to a hybrid magnetic fiber including both a hard-magnetic property and a soft-magnetic property and a method for preparing the same.

[Background Art]

[0002] Hard ferrite permanent magnet widely applied in the electrical/electronic and motor industries are roughly divided into a rare-earth magnet and a non-rare-earth magnet such as ferrite, alnico, etc. The rare-earth magnet refers to a compound between rare-earth metal and transition-metal, and has a far superior maximum magnetic energy product ((BH)max) value compared to that of the non-rare-earth permanent magnet, and thus is an indispensable material to keep up with a recent trend for light-weight, very-small and highly-efficient electronic products. However, due to a rising price of rare-earth metals and an imbalanced distribution of rare-earth resources, an attempt has been now made to carry out a rare-earth reduction, synthesize non-rare-earth magnets or synthesize alternative permanent magnets.

[0003] For example, Korean Unexamined Patent Publication No. 10-2017-0108468 (application No.: 10-2016-0032417 and applicant: Academic-Industrial Collaboration of Yonsei University) discloses a non-rare-earth permanent magnet with enhanced coercivity including a substrate and a thin film stacked body which is formed on the substrate and in which a stacked unit including a Bi thin film layer and a Mn thin film layer is repeatedly stacked and heat-treated at least twice, as well as a method for preparing the same.

[Disclosure]

[Technical Problem]

[0004] One technical object of the present invention is to provide a hybrid magnetic fiber with enhanced coercivity and saturation magnetization, and a method for preparing the same.

[0005] Another technical object of the present invention is to provide a hybrid magnetic fiber with an enhanced maximum magnetic energy product value, and a method for preparing the same.

[0006] Still another technical object of the present invention is to provide a hybrid magnetic fiber with a reduced amount of rare-earth use, and a method for preparing the same.

[0007] The technical objects of the present invention are not limited to the above.

[Technical Solution]

[0008] To solve the technical objects as described above, the present invention may provide a method for preparing a hybrid magnetic fiber.

[0009] According to one embodiment, the method for preparing a hybrid magnetic fiber may include providing a source solution including a first source material containing a rare-earth element and a second source material containing a transition-metal element, electrospinning the source solution to form a preliminary hybrid magnetic fiber including a rare-earth oxide and a transition-metal oxide, and reducing the preliminary hybrid magnetic fiber to form a hybrid magnetic fiber including magnetic crystals containing a compound of the rare-earth element and the transition-metal element and a magnetic boundary layer containing the transition-metal element.

[0010] According to one embodiment, the magnetic crystal may have a hard-magnetic property, and the magnetic boundary layer may have a soft-magnetic property.

[0011] According to one embodiment, the magnetic boundary layer may follow a magnetization behavior of the magnetic crystal.

[0012] According to one embodiment, a molar fraction of the rare-earth element in the source solution may be more than 9.290 at% and less than 10.562 at%.

[0013] According to one embodiment, the forming of the hybrid magnetic fiber may include mixing the preliminary hybrid magnetic fiber with a reducing agent, heat-treating the preliminary hybrid magnetic fiber mixed with the reducing agent, and washing the heat-treated preliminary hybrid magnetic fiber with a cleaning solution.

[0014] According to one embodiment, the preliminary magnetic fiber mixed with the reducing agent may be heat-treated at a temperature of more than 500°C and less than 800°C.

[0015] According to one embodiment, the reducing agent may contain calcium (Ca).

[0016] According to one embodiment, the cleaning solution may contain at least one of ammonium chloride (NH_4Cl)

and methanol (CH_3OH).

[0017] According to one embodiment, the source solution may further contain a crystallization source including a metal and a viscous source including a polymer.

[0018] According to one embodiment, the rare-earth element may include any one of La, Ce, Pr, Nd, Sm, or Gd.

[0019] According to one embodiment, the transition-metal element may include at least one of Fe, Co, or Ni.

[0020] To solve the technical objects as described above, the present invention may provide a hybrid magnetic fiber.

[0021] According to one embodiment, the hybrid magnetic fiber may include a plurality of magnetic crystals containing a compound of a rare-earth element and a transition-metal element, and a magnetic boundary layer disposed between the magnetic crystals adjacent to each other, surrounding the magnetic crystals, and including the transition-metal element.

[0022] According to one embodiment, a volume fraction of the magnetic boundary layer may be greater than 0 vol% and less than 10 vol% in the hybrid magnetic fiber.

[0023] According to one embodiment, the magnetic crystal may have a hard-magnetic property, and the magnetic boundary layer may have a soft-magnetic property, in which the magnetic boundary layer follows a magnetization behavior of the magnetic crystal.

[Advantageous Effects]

[0024] According to an embodiment of the present invention, a method for preparing a hybrid magnetic fiber may include providing a source solution including a first source material containing a rare-earth element and a second source material containing a transition-metal element, electrospinning the source solution to form a preliminary hybrid magnetic fiber including a rare-earth oxide and a transition-metal oxide, and reducing the preliminary hybrid magnetic fiber to form a hybrid magnetic fiber, which includes magnetic crystals containing a compound of the rare-earth element and the transition-metal element and having a hard-magnetic property and includes a magnetic boundary layer containing the transition-metal element and having a soft-magnetic property.

[0025] In addition, in the method for preparing a hybrid magnetic fiber according to the embodiment, a volume fraction of the magnetic boundary layer in the hybrid magnetic fiber can be controlled by controlling a molar fraction of the rare-earth element in the source solution, and thus a magnetic exchange-coupling effect may occur between the magnetic crystals and the magnetic boundary layer. Accordingly, there may be provided the hybrid magnetic fiber which shows an increase in saturation magnetization while maintaining high coercivity and further shows an enhanced maximum magnetic energy product ((BH)max) value, thereby providing an excellent magnetic property.

[Description of Drawings]

[0026]

FIG. 1 is a flowchart for explaining a method for preparing a hybrid magnetic fiber according to an embodiment of the present invention.

FIG. 2 is a flowchart for specifically explaining forming a hybrid magnetic fiber in the method for preparing a hybrid magnetic fiber according to an embodiment of the present invention.

FIG. 3 is a view showing a process for preparing a hybrid magnetic fiber according to an embodiment of the present invention.

FIG. 4 is a view showing a hybrid magnetic fiber according to an embodiment of the present invention.

FIG. 5 is a graph showing properties of a soft-magnetic material and a hard-magnetic material.

FIG. 6 is a graph showing properties when a magnetic exchange-coupling effect occurs between a soft-magnetic material and a hard-magnetic material.

FIGS. 7 and 8 are views showing pictures of a hybrid magnetic fiber according to Example 1 of the present invention.

FIGS. 9 to 11 are views showing pictures of comparing properties according to a temperature of heat treatment in a process of preparing a hybrid magnetic fiber according to Example 1 of the present invention.

FIG. 12 is a view showing pictures of comparing an effect of cleaning solution in a process of washing a hybrid magnetic fiber according to Example 1 of the present invention.

FIG. 13 is a view showing pictures of a hybrid magnetic fiber according to Example 2 of the present invention.

FIG. 14 is a graph showing a Sm-Co two-ingredient system.

FIG. 15 is a graph showing an effect of a molar fraction of rare-earth element contained in a source solution on a structure of a hybrid magnetic fiber according to Example 2 of the present invention.

FIGS. 16 and 17 are graphs showing an effect of a molar fraction of rare-earth element contained in a source solution on a structure of a hybrid magnetic fiber according to Example 1 of the present invention.

FIG. 18 is a graph showing properties of a hybrid magnetic fiber according to a comparative example of the present invention, to which a magnetic exchange-coupling effect does not occur.

FIG. 19 is a graph showing an effect of a volume fraction of a magnetic boundary layer on magnetic properties of a hybrid magnetic fiber according to Example 1 of the present invention.

FIG. 20 is a graph showing an effect of a volume fraction of magnetic crystals on a remanent magnetization value of a hybrid magnetic fiber according to Example 1 of the present invention.

FIG. 21 is a graph showing an effect of a volume fraction of magnetic crystals on a maximum magnetic energy product value of a hybrid magnetic fiber according to Example 1 of the present invention.

FIGS. 22 and 23 are graphs showing recoil curve tracing of hybrid magnetic fibers according to Example 1 of the present invention, which have different volume fractions of magnetic crystals and a magnetic crystal layer.

FIG. 24 is a graph showing a recoil susceptibility value of hybrid magnetic fibers according to Example 1 of the present invention, which have different volume fractions of a magnetic crystal layer.

FIGS. 25 to 27 are graphs showing a comparison of properties according to a temperature of heat treatment in a process of preparing a hybrid magnetic fiber according to Example 1 of the present invention.

FIGS. 28 is a graph showing a change in properties according to a temperature of heat treatment in a rare-earth oxide.

FIGS. 29 to 31 are pictures and graphs showing a comparison of diameters of hybrid magnetic fibers according to Examples 1 and 3 of the present invention.

[Mode for Invention]

[0027] Hereinafter, preferred embodiments of the present invention will be described in detail with reference to the accompanying drawings. However, the technical idea of the present invention is not limited to the embodiments described herein and may be embodied in other forms. The embodiments introduced herein are provided to sufficiently deliver the spirit of the present invention to those skilled in the art so that the disclosed contents may become thorough and complete.

[0028] When it is mentioned in the specification that one element is on another element, it means that the first element may be directly formed on the second element or a third element may be interposed between the first element and the second element. Further, in the drawings, the thicknesses of the membrane and areas are exaggerated for efficient description of the technical contents.

[0029] Further, in the various embodiments of the present invention, the terms such as first, second, and third are used to describe various elements, but the elements are not limited to the terms. These terms are used only to distinguish one component from another component. Accordingly, an element mentioned as a first element in one embodiment may be mentioned as a second element in another embodiment. The embodiments illustrated here include their complementary embodiments. Further, the term "and/or" in the specification is used to include at least one of the elements enumerated in the specification.

[0030] In the specification, the terms of a singular form may include plural forms unless otherwise specified. Further, the terms "including" and "having" are used to designate that the features, the numbers, the steps, the elements, or combinations thereof described in the specification are present, and are not to be understood as excluding the possibility that one or more other features, numbers, steps, elements, or combinations thereof may be present or added. In addition, the term "connection" used herein may include the meaning of indirectly connecting a plurality of components, and directly connecting a plurality of components.

[0031] Further, in the following description of the present invention, a detailed description of known functions and configurations incorporated herein will be omitted when it may make the subject matter of the present invention unnecessarily unclear.

[0032] FIG. 1 is a flowchart for explaining a method for preparing a hybrid magnetic fiber according to an embodiment of the present invention, FIG. 2 is a flowchart for specifically explaining forming a hybrid magnetic fiber in the method for preparing a hybrid magnetic fiber according to an embodiment of the present invention, FIG. 3 is a view showing a process for preparing a hybrid magnetic fiber according to an embodiment of the present invention, and FIG. 4 is a view showing a hybrid magnetic fiber according to an embodiment of the present invention.

[0033] Referring to FIGS. 1 to 4, a source solution containing a first source material and a second source material may be provided (S100). According to one embodiment, the first source material may include a rare-earth element. For example, the rare-earth element may include one of La, Ce, Pr, Nd, Sm, or Gd. According to one embodiment, the second source material may include a transition-metal element. For example, the transition-metal element may include one of Fe, Co, or Ni.

[0034] The source solution may further contain a crystallization source and a viscous source. According to one embodiment, the crystallization source may contain a metal. For example, the metal may include a metal-soluble salt such as copper (Cu), zirconium (Zr), etc. The crystallization source may enhance a degree of crystallization of a hybrid magnetic fiber 100 to be described below. According to one embodiment, the viscous source may contain a polymer. For example, the polymer may include at least one of polyvinylpyrrolidone (PVP), polyacrylonitrile (PAN), poly(vinyl acetate) (PVAC), polyvinylbutyral (PVB), poly(vinyl alcohol) (PVA) or polyethylene oxide (PEO). The viscous source may give viscosity to the source solution to control a diameter of the hybrid magnetic fiber 100 to be described below.

[0035] According to one embodiment, a molar fraction (at%) of the rare-earth element in the source solution may be controlled. Specifically, the molar fraction of the rare-earth element in the source solution may be controlled to be more than 9.290 at% and less than 10.562 at%. In this case, there may occur a magnetic exchange-coupling effect between magnetic crystals 110 and a magnetic boundary layer 120 included in the hybrid magnetic fiber 100 to be described below. In addition, the molar fraction of the rare-earth element in the source solution may be controlled to be more than 10.156 at% and less than 10.562 at%. In this case, the magnetic exchange-coupling effect generated between the magnetic crystals 110 and the magnetic boundary layer 120 included in the hybrid magnetic fiber 100 to be described below may have a maximum value. More specific description will be provided below.

[0036] The source solution may be electrospinned to form a preliminary hybrid magnetic fiber (S200). The preliminary magnetic fiber formed by electrospinning the source solution may include a rare-earth oxide and a transition-metal oxide.

[0037] According to one embodiment, the forming of the preliminary hybrid magnetic fiber may include forming a first preliminary hybrid magnetic fiber and forming a second preliminary hybrid magnetic fiber. The forming of the first preliminary hybrid magnetic fiber may be performed by a method of electrospinning the source solution. The first preliminary hybrid magnetic fiber may be made of solid ingredients of the source solution. The first preliminary hybrid magnetic fiber may include a soluble metal salt, a polymer, etc. The forming of a second preliminary hybrid magnetic fiber may be performed by a method for calcining the first preliminary hybrid magnetic fiber, that is, may be performed by a method for heat-treating the first preliminary hybrid magnetic fiber to decompose an organic matter including a polymer in the first preliminary hybrid magnetic fiber. The second preliminary hybrid magnetic fiber may include a rare-earth oxide, a transition-metal oxide, and an oxide containing a rare earth-transition metal all.

[0038] More specifically, the source solution may be injected into a syringe 10 and the source solution may be spinned by using a syringe pump 20. In this case, a tip 30 of the syringe may have an inner diameter of 0.05 to 2 mm, the syringe tip 30 and a collector for collecting the preliminary hybrid magnetic fiber may be distanced from each other by 10 to 20 cm, and the syringe pump 20 may spin the source solution at a rate of 0.3 to 0.8 mL/h. In addition, the voltage applied for electrospinning may be 16 to 23 kV. The first preliminary hybrid magnetic fiber may be formed through the above-described process.

[0039] The first preliminary hybrid magnetic fiber may be collected in an alumina crucible and heat-treated at 500 to 900°C with a normal pressure under a normal atmosphere. In this process, all organic matters including a polymer may be subject to pyrolysis. In this case, a condition for a heating rate may be 1 to 10°C per minute. The second preliminary hybrid magnetic fiber may be formed through the above-described process.

[0040] The preliminary hybrid magnetic fiber may be reduced to form the hybrid magnetic fiber 100 including the magnetic crystals 110 and the magnetic boundary layer 120 (S300). According to one embodiment, the hybrid magnetic fiber 100 may include a plurality of magnetic crystals 110, but have a structure in which the magnetic boundary layer 120 is disposed between the magnetic crystals 110 adjacent to each other and thus surrounds the magnetic crystals 110.

[0041] The magnetic crystal 110 may include a compound of the rare-earth element and the electric metal element. For example, the magnetic crystal 110 may include $Nd_2Fe_{14}B$, Sm_2Co_{17}, etc. Accordingly, the magnetic crystal 110 may have a hard-magnetic property. In contrast, the magnetic boundary layer 120 may include the transition-metal element. For example, the magnetic boundary layer 120 may include fcc-Fe, fcc-Co, etc. Accordingly, the magnetic boundary layer 120 may have a soft-magnetic property.

[0042] Unlike the above, according to another embodiment, the hybrid magnetic fiber 100 may have a chain structure in which a first single crystal 110 having a hard-magnetic property and a second single crystal 120 having a soft-magnetic property are alternately and repeatedly arranged.

[0043] In other words, the hybrid magnetic fiber 100 according to the embodiment may have one of a structure of magnetic crystal 110-magnetic boundary layer 120 or a chain structure of first single crystal 110-second single crystal 120. The structure of the hybrid magnetic fiber 100 may be determined according to a condition for the electrospinning process described above, a condition for heat treatment in the heat treatment reduction step to be described below, a volume ratio of a hard-magnetic property material and a soft-magnetic property material in the hybrid magnetic fiber 100, and the like. Specifically, if the hybrid magnetic fiber 100 is prepared to have a diameter of less than 500 nm by controlling the condition for electrospinning process, the hybrid magnetic fiber 100 may be formed to have the chain structure of first single crystal 110-second single crystal 120. In addition, if a volume of the soft-magnetic property material in the hybrid magnetic fiber 100 is 10 vol% or more, the hybrid magnetic fiber 100 may be formed to have the chain structure of first single crystal 110-second single crystal 120.

[0044] The hybrid magnetic fiber 100 may be applied to different fields of industry according to a shape of the structure to be formed. For example, if the hybrid magnetic fiber 100 has the structure of magnetic crystal 110-magnetic boundary layer 120, the hybrid magnetic fiber 100 may be subject to sintering and used in a high-power product in the form of sintered magnet. In particular, the hybrid magnetic fiber may be used in various high-tech equipments such as driving motors for hybrid electric vehicles (HEV) and electric vehicles (EV), small motors for vehicles, VCMs for hard disks, speakers for mobile phones, small parts in industrial robots, MRI, etc.

[0045] In contrast, if the hybrid magnetic fiber 100 has the chain structure of first single crystal 110-second single crystal 120, the hybrid magnetic fiber 100 may be mixed with a binder material and molded to be used as a bond-based magnet (plastic magnets and rubber magnets). The above magnet may have a low magnetic property compared to sintered magnets, but may have high processability, earthquake resistance, and impact resistance, and thus can be used for door packing of refrigerators, paperweights on bulletin boards, various stationery, etc.

[0046] According to one embodiment, the forming of the hybrid magnetic fiber 100 (S300) may include mixing the preliminary hybrid magnetic fiber with a reducing agent (S310), heat-treating the preliminary hybrid magnetic fiber mixed with the reducing agent (S320), and washing the heat-treated preliminary hybrid magnetic fiber with a cleaning solution (S330). In other words, the preliminary hybrid magnetic fiber 100 may be mixed with a reducing agent and subject to heat treatment so as to form the hybrid magnetic fiber 100.

[0047] The reducing agent may include calcium (Ca). For example, the reducing agent may include CaH_2. In this case, the hybrid magnetic fiber 100 may be easily formed. Specifically, rare-earth elements may have a very small oxidation energy and thus maintain the most stable phase in the form of oxide. Accordingly, a high temperature of 1500°C or higher or a hydrogen atmosphere may be required to reduce a rare-earth oxide into a metal, thereby causing difficulty in a process. However, calcium (Ca) may have a smaller oxidation energy than that of the rare-earth elements. Thus, if calcium is used as a reducing agent, a rare-earth oxide may be easily reduced into metal at a relatively low temperature of heat treatment (for example, 500 to 800°C) and under a non-hydrogen atmosphere.

[0048] It may be possible to control the temperature of heat treatment for the preliminary hybrid magnetic fiber mixed with the reducing agent. Specifically, the preliminary hybrid magnetic fiber mixed with the reducing agent may be heat-treated at a temperature of more than 500°C and less than 800°C. In this case, the hybrid magnetic fiber 100 may be easily formed. In contrast, if the preliminary hybrid magnetic fiber mixed with the reducing agent is heat-treated at a temperature of 500°C or less, there may be a problem in that the temperature is too low to carry out reduction. In addition, if the preliminary hybrid magnetic fiber mixed with the reducing agent is heat-treated at a temperature of 800°C or higher, the hybrid magnetic fiber 100 may not have a form of fiber, but may be transformed into a form of particle.

[0049] The cleaning solution may contain at least one of ammonium chloride (NH_4Cl) and methanol (CH_3OH). In this case, the hybrid magnetic fiber 100 may be easily formed. Specifically, if the preliminary hybrid magnetic fiber is reduced by using a reducing agent containing calcium (Ca), calcium oxide (CaO) may be formed on a surface of metal, into which a rare-earth oxide is reduced. Accordingly, a process of removing calcium oxide (CaO) may be required. The existing process of removing calcium oxide (CaO) has used a washing solution in which acetic acid or hydrochloric acid is mixed with ultrapure water. In this case, there may be a problem in that an acid solution causes a fatal effect such as corrosion, oxidation, etc., even on a magnetic phase. However, a washing solution containing at least one of ammonium chloride (NH_4Cl) and methanol (CH_3OH) may easily remove calcium oxide (CaO) without affecting the magnetic phase.

[0050] According to one embodiment, a volume fraction (vol%) of the magnetic boundary layer 120 may be controlled in the hybrid magnetic fiber 100. Specifically, a volume fraction of the magnetic boundary layer 120 may be controlled to be greater than 0 vol% and less than 10 vol% in the hybrid magnetic fiber 100. In this case, the magnetic boundary layer 120 may follow a magnetization behavior of the magnetic crystal 110. In other words, a magnetic exchange-coupling effect may occur between the magnetic crystals 110 and the magnetic boundary layer 120. In addition, a volume fraction of the magnetic boundary layer 120 may be controlled to be greater than 0 vol% and less than 3 vol% in the hybrid magnetic fiber 100. In this case, the magnetic exchange coupling effect generated between the magnetic crystals 110 and the magnetic boundary layer 120 may have a maximum value.

[0051] FIG. 5 is a graph showing properties of a soft-magnetic material and a hard-magnetic material, and FIG. 6 is a graph showing properties when a magnetic exchange-coupling effect occurs between a soft magnetic material and a hard magnetic material.

[0052] Referring to FIGS. 5 and 6, a soft-magnetic material may have properties of showing a relatively high saturation magnetization (Ms) and a relatively low coercivity (H_C) as shown in (a) of FIG. 5. In contrast, a hard-magnetic material may have properties of showing a relatively high coercivity (H_C) and a relatively low saturation magnetization (Ms) as shown in (b) of FIG. 5. However, if a magnetic exchange-coupling effect occurs between the soft-magnetic material and the hard-magnetic material, this case may have properties of showing both a high coercivity (H_C) and a high saturation magnetization (M_S) as shown in FIG. 6. In result, a material showing a magnetic exchange-coupling effect between the hard-magnetic material and the soft-magnetic material may have an excellent magnetic property and thus can be easily used as a permanent magnet.

[0053] As described above, the hybrid magnetic fiber 100 according to the embodiment may have a magnetic exchange-coupling effect generated between the magnetic crystals 110 having a hard-magnetic property and the magnetic boundary layer 120 having a soft-magnetic property, which are included in the hybrid magnetic fiber 100. For this purpose, a volume fraction of the magnetic boundary layer 120 in the hybrid magnetic fiber 100 may be controlled. In addition, a volume fraction of the magnetic boundary layer 120 in the hybrid magnetic fiber 100 may be controlled by a molar fraction of the rare-earth element in the source solution. A molar fraction of the rare-earth element in the source solution according to a volume fraction of the magnetic boundary layer 120 in the hybrid magnetic fiber 100 may be calculated through

<Equation 1> below.

<Equation 1>

$$RE[unit:at.\%] = 100^* \frac{\frac{\rho_{hard}x_{hard}m_{RE}}{MW_{hard}}}{\left\{\frac{\rho_{hard}x_{hard}m_{RE}}{MW_{hard}} + \frac{\rho_{hard}x_{hard}m_{TM}}{MW_{hard}}\right\} + \frac{\rho_{soft}(1-x_{hard})}{MW_{soft}}}$$

[0054] (RE (at.%) : Molar fraction of rare-earth element in source solution, ρ_{hard}: Density of magnetic crystals, x_{hard}: Volume fraction (0.0-1.0) of magnetic crystals in hybrid magnetic fiber, m_{RE}: Number of atoms of rare-earth element in magnetic crystal (Ex: m_{RE}=2 in Sm_2Co_{17}), MW_{hard}: Molecular weight of magnetic crystal, ρ_{soft}: Density of magnetic boundary layer, m_{TM}: Number of atoms of transition-metal element in magnetic crystal (Ex: m_{TM}=17 in Sm_2Co_{17}), MW_{soft}: Molecular weight of magnetic boundary layer)

[0055] In other words, as a molar fraction of the rare-earth element in the source solution is controlled, a volume fraction of the magnetic boundary layer 120 in the hybrid magnetic fiber 100 may be controlled, and thus a magnetic exchange-coupling effect may occur between the magnetic crystals 110 and the magnetic boundary layer 120. Specifically, if a molar fraction of the rare-earth element in the source solution is controlled to be greater than 9.290 at% and less than 10.562 at%, a volume fraction of the magnetic boundary layer 120 in the hybrid magnetic fiber 100 may be controlled to be greater than 0 vol% and less than 10 vol%. In this case, a magnetic exchange-coupling effect may occur between the magnetic crystals 110 and the magnetic boundary layer 120. In result, the hybrid magnetic fiber 100 according to the embodiment may show high magnetic properties and thus can be easily used as a permanent magnet. In other words, the hybrid magnetic fiber 100 according to the embodiment may show high magnetic properties through mixing of a hard-magnetic material and a soft-magnetic material, and thus reduce the use of rare-earth materials for preparing a permanent magnet.

[0056] Unlike the method for preparing the hybrid magnetic fiber according to the embodiment described above, a simple mixing method, a coating method, a deposition method, a bulk process, a plasma process and the like have been conventionally used to mix a hard-magnetic material and a soft-magnetic material.

[0057] The simple mixing method is a method for physically bonding hard-magnetic nano powders and soft-magnetic nano powders, and has a disadvantage in that an additional process such as sintering, etc., needs to be performed to generate the magnetic exchange-coupling effect.

[0058] The coating method is a technique for coating a soft-magnetic material onto a hard-magnetic material to form a material having a core-shell structure, and a sol-gel coating method is typically used. The sol-gel coating method is very vulnerable to oxidation on a surface of nano powders, such as a chemical reaction of a hard-magnetic material in a process of heat treatment in air and hydrogen heat treatment for sol formation and reduction, oxidation of the hard-magnetic material in a process of heat treatment for removing organic matters, etc., and thus ferrite, a form of oxide, is mainly used. Accordingly, there is a problem in that it is difficult to expect a higher magnetic property than a commercial hard ferrite.

[0059] The deposition method is a technique for preparing a composite powder by coating a soft-magnetic material onto a surface of a hard-magnetic material through electroless or electrolytic deposition, in which oxidation and surface defects of the hard-magnetic material may occur from a process of immersing the hard-magnetic material in an acidic solution containing hydrochloric acid (HCl), or from a process of using a basic plating solution containing an ammonia solution. Accordingly, the use of deposition method is limited only to ferrite having a stable oxide type. If a soft-magnetic coating layer prepared as a result of performing deposition is an oxide, there is a problem in that an additional reduction heat treatment process needs to be accompanied.

[0060] The bulk process includes a technique for preparing a hard-magnetic alloy and a soft-magnetic alloy from a high-purity metal ingot, or a technique for precipitating a hybrid structure of a hard-magnetic material and a soft-magnetic material through subsequent heat treatment of an amorphous hard-magnetic material. A high magnetic property can be expected, but there is a problem in that a range of use for bonded magnet is limited due to low coercivity.

[0061] The plasma process may generate nano-sized hard-magnetic and soft-magnetic composite powders under an inert atmosphere, but requires a high-quality heat source of 5,000 to 10,000 K for vaporization and dissolution of the powders. It is also difficult to control a size and an amount, and there may be a problem of reactivity between the nano-powder and gas during a process of powder collection.

[0062] However, the method for preparing the hybrid magnetic fiber according to an embodiment of the present invention may include providing the source solution including a first source material containing a rare earth element and a second source material containing a transition metal element, electrospinning the source solution to form the preliminary hybrid magnetic fiber including a rare-earth oxide and a transition-metal oxide, and reducing the preliminary hybrid magnetic fiber to form the hybrid magnetic fiber 100, which includes the magnetic crystals 110 containing a compound of the rare-earth element and the transition-metal element and having a hard-magnetic property, and includes the magnetic boundary layer 120 containing the transition-metal element and having a soft-magnetic property.

[0063] In addition, the method for preparing the hybrid magnetic fiber according to the embodiment, a volume fraction of the magnetic boundary layer 120 in the hybrid magnetic fiber 100 may be controlled by controlling a molar fraction of the rare-earth element in the source solution, and thus a magnetic exchange-coupling effect may occur between the magnetic crystals 110 and the magnetic boundary layer 120. Accordingly, there may be provided the hybrid magnetic fiber which shows an increase in saturation magnetization while maintaining high coercivity and further shows an enhanced maximum magnetic energy product ((BH)max) value, thereby providing an excellent magnetic property.

[0064] According to an embodiment of the present invention, the hybrid magnetic fiber and the method for preparing the same have been described. Hereinafter, specific experimental embodiments and the results of evaluating properties will be described with regard to the hybrid magnetic fiber according to an embodiment of the present invention and the method for preparing the same.

<u>Preparing of hybrid magnetic fiber according to Example</u> 1

[0065] A solution, in which samarium (III) nitrate hexahydrate ($Sm(NO_3)_36H_2O$) and cobalt (II) nitrate hexahydrate ($Co(NO_3)_26H_2O$) were mixed in 4 mL of ultrapure water, was mixed with a solution, in which 0.4 g of PVP having a molecular weight of 1,300,000 was dissolved in 6 mL of ethanol, so as to prepare a source solution.

[0066] The prepared source solution was inserted into a syringe for electrospinning, and the solution was continuously pushed at a rate of 0.3 to 0.8 mL/h by using a syringe pump. In this case, a tip portion of the syringe and a collector for collecting the spinned fiber were distanced from each other by 15 cm, and high voltage (16-23 kV) was applied so that the source solution could be spinned by a potential difference. The material deposited in the collector was collected in an alumina (Al_2O_3) crucible and heat-treated under an air atmosphere at a temperature of about 700°C for three hours to decompose all organic matters including polymers. In this process, a preliminary hybrid magnetic fiber containing a rare earth oxide-transition metal oxide of $SmCoO_3$-Co_3O_4 was obtained.

[0067] The preliminary hybrid magnetic fiber was mixed with CaH_2 at a volume ratio of 1:1, heat-treated and reduced under an inert atmosphere at a temperature of about 700°C for three hours, and washed with ammonium chloride and methanol, so as to prepare a hybrid magnetic fiber according to a first embodiment including Sm_2Co_{17} magnetic crystals having a hard-magnetic property and an fcc-Co magnetic boundary layer having a soft-magnetic property.

[0068] In addition, in order to control a volume fraction of the Sm_2Co_{17} magnetic crystals in the hybrid magnetic fiber according to the first embodiment, a molar fraction of the samarium element in the source solution was controlled and calculated through <Equation 2> below, and thus the calculated results are summarized in <Table 1>.

[Equation 2]

$$Sm[unit:at.\%] = 100^* \frac{\frac{\rho_{Sm_2Co_{17}} x_{Sm_2Co_{17}} m_{Sm}}{MW_{Sm_2Co_{17}}}}{\left\{\frac{\rho_{Sm_2Co_{17}} x_{Sm_2Co_{17}} m_{Sm}}{MW_{Sm_2Co_{17}}} + \frac{\rho_{Sm_2Co_{17}} x_{Sm_2Co_{17}} m_{Co}}{MW_{Sm_2Co_{17}}}\right\} + \frac{\rho_{fcc-Co}(1 - x_{Sm_2Co_{17}})}{MW_{fcc-Co}}}$$

$$= \frac{8.8476x_{Sm_2Co_{17}}}{1 - 0.1623x_{Sm_2Co_{17}}}$$

[0069] (SM (at%): Molar fraction of rare-earth element in source solution, $\rho_{Sm2Co17}$: Density of Sm_2Co_{17} magnetic crystals, $x_{Sm2Co17}$: Volume fraction (0.0~1.0) of Sm_2Co_{17} magnetic crystals in hybrid magnetic fiber, m_{Sm}: Number of atoms of rare-earth element in magnetic crystal, $MW_{Sm2Co17}$: Molecular weight of magnetic crystal. ρ_{Co}: Density of magnetic boundary layer, m_{Co}: Number of atoms of transition-metal element in magnetic crystal, MW_{Co}: Molecular weight of magnetic boundary layer)

[Table 1]

Volume fraction of magnetic crystals in hybrid magnetic fiber (Sm_2Co_{17} vol%)	Molar fraction of rare-earth element in source solution (Sm at%)
100	10.562
99	10.409
97	10.156
95	9.906
90	9.290
80	8.101
50	4.803
30	2.786
10	0.885
0	0

Preparing of hybrid magnetic fiber according to Example 2

[0070] A solution, in which neodymium (III) nitrate hexahydrate ($Nd(NO_3)_36H_2O$) and iron (III) nitrate nonahydrate ($Fe(NO_3)_39H_2O$) were mixed in 4.5 mL of ultrapure water, was mixed with a solution, in which 0.6 g of PVP having a molecular weight of 1,300,000 was dissolved in 3 mL of ethanol, so as to prepare a source solution. In addition, boric acid (H_3BO_3) was further mixed in such an amount that is a half of the number of moles of neodymium (III) nitrate hexahydrate.

[0071] The prepared source solution was inserted into a syringe for electrospinning, and the solution was continuously pushed at a rate of 0.3 to 0.8 mL/h by using a syringe pump. In this case, a tip portion of the syringe and a collector for collecting the spinned fiber were distanced from each other by 18 cm, and high voltage (16-23 kV) was applied so that the source solution could be spinned by a potential difference. The material deposited in the collector was collected in an alumina (Al_2O_3) crucible and heat-treated under an air atmosphere at a temperature of about 700°C for three hours to decompose all organic matters including polymers. In this process, a preliminary hybrid magnetic fiber containing a rare earth oxide-transition metal oxide of $NdFeO_3$-$NdBO_3$-Fe_2O_3 was obtained.

[0072] The preliminary hybrid magnetic fiber was mixed with CaH_2 at a volume ratio of 1:1, heat-treated and reduced under an inert atmosphere at a temperature of about 700°C for three hours, and washed with ammonium chloride and methanol, so as to prepare a hybrid magnetic fiber according to a second embodiment including $Nd_2Fe_{14}B$ magnetic crystals having a hard-magnetic property and an fcc-Fe magnetic boundary layer having a soft-magnetic property.

[0073] In addition, in order to control a volume fraction of the $Nd_2Fe_{14}B$ magnetic crystals in the hybrid magnetic fiber according to the second embodiment, a molar fraction of the neodymium element in the source solution was controlled and calculated through <Equation 3> below, and thus the calculated results are summarized in <Table 2>.

<Equation 3>

$$Nd[unit:at.\%] = 100 * \frac{\frac{\rho_{Nd_2Fe_{14}B} x_{Nd_2Fe_{14}B} m_{Nd}}{MW_{Nd_2Fe_{14}B}}}{\left\{\frac{\rho_{Nd_2Fe_{14}B} x_{Nd_2Fe_{14}B} m_{Nd}}{MW_{Nd_2Fe_{14}B}} + \frac{\rho_{Nd_2Fe_{14}B} x_{Nd_2Fe_{14}B} m_{Fe}}{MW_{Nd_2Fe_{14}B}}\right\} + \frac{\rho_{fcc-Fe}(1 - x_{Nd_2Fe_{14}B})}{MW_{fcc-Fe}}}$$

[0074] (Nd (at%): Molar fraction of rare-earth element in

$$= \frac{0.0995x_{Nd_2Fe_{14}B}}{1-0.2043x_{Nd_2Fe_{14}B}}$$

source solution, $\rho_{Nd2Fe14B}$: Density of $Nd_2Fe_{14}B$ magnetic crystal, $x_{Nd2Fe14B}$: Volume fraction (0.0~1.0) of $Nd_2Fe_{14}B$ magnetic crystals in hybrid magnetic fiber, m_{Nd}: Number of atoms of rare-earth element in magnetic crystal, $MW_{Nd2Fe14B}$: Molecular weight of magnetic crystal. ρ_{Fe}: Density of magnetic boundary layer, m_{Fe}: Number of atoms of transition-metal element in magnetic crystal, MW_{Fe}: Molecular weight of magnetic boundary layer)

[Table 2]

Volume fraction of magnetic crystals in hybrid magnetic fiber ($Nd_2Fe_{14}B$ vol%)	Molar fraction of rare-earth element of source solution (Nd at%)
100	12.505
99	12.348
97	12.037
95	11.729
90	10.973
80	9.515
50	5.541
30	3.180
10	1.016
0	0

[0075] In addition, a composition of the hybrid magnetic fiber according to above Examples 1 and 2 are summarized in <Table 3> below.

[0076]

[Table 3]

Classification	Magnetic crystal	Magnetic boundary layer
Example 1	Sm_2Co_{17}	Co
Example 2	$Nd_2Fe_{14}B$	Fe

Preparing of hybrid magnetic fiber according to Example 3

[0077] The hybrid magnetic fiber according to above Example 1 was prepared to have a diameter of 250 nm or less, thereby preparing a hybrid magnetic fiber according to above Example 3 having a chain structure of hard magnetic property single crystal-soft magnetic property single crystal.

[0078] A structure of the hybrid magnetic fiber according to above Examples 1 to 3 is summarized in <Table 4> below.

[Table 4]

Classification	Structure
Example 1	Structure of magnetic crystal-magnetic boundary layer
Example 2	Structure of magnetic crystal-magnetic boundary layer
Example 3	Chain structure of single crystal-single crystal

[0079] FIGS. 7 and 8 are views showing pictures of a hybrid magnetic fiber according to Example 1 of the present invention.

[0080] Referring to FIGS. 7 and 8, a scanning electron microscope (SEM) picture was taken of the hybrid magnetic fiber according to above Example 1, which was formed by controlling a molar fraction of the rare-earth element in the source solution to be 10.56 at%, 0 at%, 9.91 at% and 4.80 at%, and was shown in (a) of FIG. 7, (b) of FIG. 7, (a) of FIG. 8, and (b) of FIG. 8, respectively. As can be understood from FIGS. 7 and 8, it was confirmed that the hybrid magnetic fiber according to above Example 1 is formed in the shape of a fiber having a diameter of about 500 nm.

[0081] FIGS. 9 to 11 are views showing pictures of comparing properties according to a temperature of heat treatment in a process of preparing a hybrid magnetic fiber according to Example 1 of the present invention.

[0082] Referring to FIGS. 9 to 11, an SEM picture was taken of the hybrid magnetic fiber according to above Example 1, which was formed by controlling a temperature of heat treatment to be 400°C, 500°C, 600°C, 700°C, 750°C and 800°C in the step of reducing the preliminary hybrid magnetic fiber, and was shown in (a) of FIG. 9, (b) of FIG. 9, (a) of FIG. 10, (b) of FIG. 10, (a) of FIG. 11 and (b) of FIG. 11, respectively.

[0083] As can be understood from (a) and (b) of FIG. 9, it was confirmed that the rare-earth oxide is not easily reduced if a temperature of heat treatment is 400°C and 500°C in the reducing step. In addition, as can be understood from (a) and (b) of FIG. 11, it was confirmed that a shape of fiber is not maintained and deformed into a shape of particle, if a temperature of heat treatment is 750°C and 800°C in the reducing step. In contrast, as can be understood from (a) and (b) of FIG. 10, it was confirmed that the rare-earth oxide is easily reduced and thus the hybrid magnetic fiber is easily formed if a temperature of heat treatment is 600°C and 700°C in the reducing step.

[0084] FIG. 12 is a view showing pictures of comparing an effect of cleaning solution in a process of washing a hybrid magnetic fiber according to Example 1 of the present invention.

[0085] Referring to (a) and (b) of FIG. 12, in the process of washing the hybrid magnetic fiber according to above Example 1, a case of washing with a cleaning solution according to an embodiment mixed with ammonium chloride and methanol is shown in (a) of FIG. 12, and a case of washing with an existing cleaning solution mixed with ultrapure water and weak acid is shown in (b) of FIG. 12. As can be understood from (a) and (b) of FIG. 12, in case of washing with the existing cleaning solution, by-products remain on a surface of fiber so as to reduce magnetic properties. In contrast, in case of washing with the cleaning solution according to the embodiment, it was confirmed that by-products excluding the magnetic fiber are selectively removed to obtain magnetic properties reaching a theoretical value.

[0086] FIG. 13 is a view showing pictures of a hybrid magnetic fiber according to Example 2 of the present invention.

[0087] Referring to (a) to (c) of FIG. 13, an SEM picture was taken of the hybrid magnetic fiber according to above Example 2, which was formed by controlling a molar fraction of the rare-earth element in the source solution to be 12.5 at%, 3.18 at% and 0 at%, and was shown in (a) to (c) of FIG. 13, respectively. As can be understood from (a) to (c) of FIG. 13, it was confirmed that the hybrid magnetic fiber is easily formed even if Nd is used as a rare-earth element and Fe is used as a transition-metal element.

[0088] FIG. 14 is a graph showing an Sm-Co two-ingredient system.

[0089] Referring to FIG. 14, a state of a Sm-Co compound according to a molar fraction (at%) of Sm in the Sm-Co compound and temperature (°C) is shown. As can be understood from FIG. 14, it was confirmed that a hard-magnetic property and a soft-magnetic property coexist if a molar fraction of Sm in the Sm-Co compound is less than 10.6 at%.

[0090] FIG. 15 is a graph showing an effect of a molar fraction of rare-earth element contained in a source solution on a structure of a hybrid magnetic fiber according to Example 2 of the present invention.

[0091] Referring to (a) to (c) of FIG. 15, a relative intensity (a.u.) according to 2θ (degree) was measured with regard to each of the hybrid magnetic fibers according to above Example 2, which was formed by controlling a molar fraction of the rare-earth element (Nd) in the source solution to be 12.5 at%, 3.18 at% and 0 at%, so that an X-ray diffraction analysis was shown. As can be understood from (a) of FIG. 15, it was confirmed that only the hard-magnetic property of $Nd_2Fe_{14}B$ appears if a molar fraction of the rare-earth element in the source solution is 12.5 at%. In addition, as can be understood from (c) of FIG. 15, it was confirmed that only the soft-magnetic property of fcc-Fe appears if a molar fraction of the rare-earth element in the source solution is 0 at%. However, as can be understood from (b) of FIG. 15, it was confirmed that both the hard-magnetic property of $Nd_2Fe_{14}B$ and the soft-magnetic property of fcc-Fe appear if a molar fraction of the rare-earth element in the source solution is 3.15 at%.

[0092] FIGS. 16 and 17 are graphs showing an effect of a molar fraction of rare-earth element contained in a source solution on a structure of a hybrid magnetic fiber according to Example 1 of the present invention.

[0093] Referring to FIGS. 16 and 17, a relative intensity (a.u.) according to 2θ (degree) was measured with regard to each of the hybrid magnetic fibers according to above Example 2, which was formed by controlling a molar fraction of the rare-earth element (Sm) in the source solution to be 10.56 at%, 0 at%, 9.91 at% and 4.80 at%, so that an X-ray diffraction was analyzed and shown in (a) of FIG. 16, (b) of FIG. 16, (a) of FIG. 17, and (b) of FIG. 17, respectively.

[0094] As can be understood from (a) of FIG. 16, it was confirmed that only the hard-magnetic property of Sm_2Co_{17} appears if a molar fraction of the rare-earth element in the source solution is 10.56 at%. In addition, as can be understood from (b) of FIG. 16, it was confirmed that only the soft-magnetic property of fcc-Fe appears if a molar fraction of the rare-earth element in the source solution is 0 at%. However, as can be understood from (a) and (b) of FIG. 17, it was confirmed that both the hard-magnetic property of Sm_2Co_{17} and the soft-magnetic property of fcc-Fe appear if a molar fraction of the rare-earth element in the source solution is 9.91 at% and 4.80 at%.

[0095] FIG. 18 is a graph showing properties of a hybrid magnetic fiber according to a comparative example of the present invention, to which a magnetic exchange-coupling effect does not occur.

[0096] Referring to FIG. 18, magnetization (emu/g) was measured depending on an applied field (kOe) of the hybrid magnetic fiber according to the comparative example of the present invention, in which the Sm_2Co_{17} hard-magnetic material and the fcc-Co soft-magnetic material are simply mixed in a volume ratio of 50 vol%: 50 vol%, so that a hysteresis curve was shown. As can be understood from FIG. 18, the hybrid magnetic fiber according to above Example 1, in which a volume fraction of the Sm_2Co_{17} magnetic crystal and the fcc-Co magnetic boundary layer was controlled to be 50 vol%: 50 vol%, showed a kink phenomenon, and thus it was confirmed that a magnetic exchange-coupling effect does not occur.

[0097] FIG. 19 is a graph showing an effect of a volume fraction of a magnetic boundary layer on magnetic properties of a hybrid magnetic fiber according to Example 1 of the present invention.

[0098] Referring to FIG. 19, magnetization (emu/g) was measured depending on an applied field (Oe) of the hybrid magnetic fiber according to above Example 1, in which a volume fraction of the fcc-Co magnetic boundary layer is controlled, so that a hysteresis curve was shown. As can be confirmed from FIG. 19, the hybrid magnetic fiber according to Example 1 of the present invention did not show a kink phenomenon in the hysteresis curve unlike the hybrid magnetic fiber according to the comparative example shown in FIG. 18, so that it was confirmed that a magnetic exchange-coupling effect occurs.

[0099] In addition, the magnetic properties of the hybrid magnetic fiber according to above Example 1, which have different volume fractions of fcc-Co magnetic boundary layer, are summarized in <Table 5> below.

[Table5]

Volume fraction of Fcc-Co magnetic boundary layer (vol %)	Saturation magnetization M_s (emu/g)	Remanent magnetization M_r (emu/g)	Magnetic susceptibility M_r/M_s (%)	Coercivity H_{ci} (Oe)	Maximum magnetic energy product $(BH)_{max}$ (M GOe)
0	84.390	58.509	69.332	7044.6	7.001
0.3	88.176	60.696	68.835	6953.3	N/A
1	87.265	59.559	68.251	6953.7	7.577
1.5	87.550	59.756	68.253	6741.5	N/A
3	87.887	58.706	66.797	6513.4	7.429
5	97.310	63.135	64.880	6193.0	7.208
7	98.377	62.070	63.094	5721.2	6.398
10	98.760	60.329	61.087	5128.0	6.010
20	99.444	54.478	54.783	3672.1	N/A
30	109.350	52.182	47.720	2526.2	N/A
50	124.670	47.231	37.885	1208.9	N/A
70	138.460	40.602	29.324	604.1	N/A
100	164.600	25.245	15.337	162.5	0.401

[0100] As can be understood from <Table 5>, it was confirmed that the hybrid magnetic fiber according to above Example 1 shows the highest maximum magnetic energy product ($(BH)_{max}$) value if a volume fraction of the fcc-Co magnetic boundary layer is 1 vol%. Accordingly, it was understood that a magnetic exchange-coupling effect is maximally implemented between Sm_2Co_{17} magnetic crystals and fcc-Co magnetic boundary layer if a volume fraction of the fcc-Co magnetic boundary layer is 1 vol%.

[0101] Theoretically, in order to generate the magnetic exchange-coupling force between the hard-magnetic material and the soft-magnetic material, a size of the soft-magnetic material needs to be smaller than such a value that is twice as much as a domain-wall width of a hard-magnetic material domain boundary. A theoretical size of the fcc-Co magnetic boundary layer required to show the magnetic exchange-coupling effect between the Sm_2Co_{17} magnetic crystals and the fcc-Co magnetic boundary layer was about 20.0 nm, which was less than about 5 at% if calculated as a volume fraction. Thus, it can be understood that the size substantially corresponds to experimental data of the present invention.

[0102] FIG. 20 is a graph showing an effect of a volume fraction of magnetic crystals on a remanent magnetization value of a hybrid magnetic fiber according to Example 1 of the present invention.

[0103] Referring to FIG. 20, a remanent magnetization value (Remanence, M_r (emu/g)) of the hybrid magnetic fiber according to above Example 1, in which a volume fraction of the Sm_2Co_{17} magnetic crystal is controlled, was measured and shown. As can be understood from FIG. 20, it was confirmed that a remanent magnetization value is higher than a remanent magnetization value of Sm_2Co_{17} single phase, if a volume fraction of the Sm_2Co_{17} magnetic crystal is 90 vol% or more.

[0104] FIG. 21 is a graph showing an effect of a volume fraction of magnetic crystals on a maximum magnetic energy product value of a hybrid magnetic fiber according to Example 1 of the present invention.

[0105] Referring to FIG. 21, a maximum magnetic energy product ($(BH)_{max}$ (MGOe)) value of the hybrid magnetic fiber according to above Example 1, in which a volume fraction of the Sm_2Co_{17} magnetic crystals is controlled, was measured and shown. As can be understood from FIG. 21, it was confirmed that a maximum magnetic energy product value is the highest as 7.577 MGOe if a volume fraction of the Sm_2Co_{17} magnetic crystal is 99 vol%.

[0106] As can be understood from FIGS. 19 to 21, it can be understood that the hybrid magnetic fiber according to above Example 1 has a magnetic exchange-coupling effect easily generated between the Sm_2Co_{17} magnetic crystals and the fcc-Co magnetic boundary layer if a volume fraction of the fcc-Co magnetic boundary layer is more than 0 vol% and less than 3 vol%.

[0107] FIGS. 22 and 23 are graphs showing recoil curve tracing of hybrid magnetic fibers according to Example 1 of the present invention, which have different volume fractions of magnetic crystals and a magnetic crystal layer.

[0108] Referring to FIGS. 22 and 23, magnetization (emu/g) according to Applied Field (Oe) was measured for each of the cases in which a volume fraction of the Sm_2Co_{17} magnetic crystals and the fcc-Co magnetic crystal layer is 97 vol%: 3 vol%, 95 vol%: 5 vol%, and 70 vol%: 30 vol%, and recoil curve tracing was shown in (a) of FIG. 22, (b) of FIG. 22 and (c) of FIG. 23.

[0109] As can be understood from (a) and (b) of FIG. 22, it was confirmed that the hybrid magnetic fiber according to above Example 1 shows a closed loop if a volume fraction of the Sm_2Co_{17} magnetic crystals and the fcc-Co magnetic crystal layer is 97 vol%: 3 vol% and 95 vol%: 5 vol%. In contrast, as can be understood from FIG. 23, it was confirmed that the hybrid magnetic fiber according to above Example 1 shows an opened loop if a volume fraction of the Sm_2Co_{17} magnetic crystals and the fcc-Co magnetic crystal layer is 70 vol%: 3 vol%. This means that the hybrid magnetic fiber with a closed loop shows a magnetic exchange-coupling effect between the Sm_2Co_{17} magnetic crystals and the fcc-Co magnetic crystal layer, but the hybrid magnetic fiber with an opened loop does not show a magnetic exchange-coupling effect between the Sm_2Co_{17} magnetic crystals and the fcc-Co magnetic crystal layer.

[0110] FIG. 24 is a graph showing a recoil susceptibility value of hybrid magnetic fibers according to Example 1 of the present invention, which have different volume fractions of a magnetic crystal layer.

[0111] Referring to FIG. 24, dM/dH (emu/(g.Oe)) depending on H (kOe) was measured for each of the hybrid magnetic fibers according to above Example 1, in which a volume fraction of the fcc-Co magnetic crystal layer is more than 1 vol% (Co-excess-1), more than 3 vol% (Co-excess-3), more than 5 vol% (Co-excess-5), and more than 30 vol% (Co-excess-30), and recoil susceptibility values were shown.

[0112] As can be understood from FIG. 24, it was confirmed that one peak appears to the hybrid magnetic fiber according to above Example 1, if a volume fraction of the fcc-Co magnetic crystal layer is more than 1 vol% (Co-excess-1), more than 3 vol% (Co-excess-3), and more than 5 vol% (Co-excess-5) . However, it was confirmed that two peaks appear to a portion of about -7 kOe and -2.5 kOe in the hybrid magnetic fiber according to above Example 1, if a volume fraction of the fcc-Co magnetic crystal layer is more than 30 vol% (Co-excess-30). In the graph of showing a recoil susceptibility value, one peak means that a magnetic exchange-coupling effect appears between the Sm_2Co_{17} magnetic crystals and the fcc-Co magnetic crystal layer, and two peaks mean that a magnetic exchange-coupling effect does not appear between the Sm_2Co_{17} magnetic crystals and the fcc-Co magnetic crystal layer.

[0113] FIGS. 25 to 27 are graphs showing a comparison of properties according to a temperature of heat treatment in a process of preparing a hybrid magnetic fiber according to Example 1 of the present invention.

[0114] Referring to FIGS. 25 to 27, a relative intensity (a.u.) depending on 2theta (deg.) was measured for each of the hybrid magnetic fibers according to above Example 1, which were formed by controlling a temperature of heat treatment to be 400°C, 500°C, 600°C, 700°C, 750°C and 800°C in the step of reducing the preliminary hybrid magnetic fiber, so that an X-ray diffraction analysis was shown. Hybrid magnetic fibers, which were heat-treated at a temperature of 400°C, 500°C, 600°C, and 700°C, are shown in FIG. 25, hybrid magnetic fibers, which were heat-treated at a temperature of 700°C, 750°C, and 800°C, are shown in FIG. 26, and an enlarged graph of portion A of FIG. 26 is shown in FIG. 27.

[0115] As can be understood from FIGS. 25 to 27, it was confirmed that the rare-earth oxide is not easily reduced if a temperature of heat treatment is 400°C and 500°C in the reducing step, and thus a mixed structure between the

Sm_2Co_{17} magnetic crystals and the fcc-Co magnetic crystal layer is not measured. In addition, it was confirmed that a mixed structure between the Sm_2Co_{17} magnetic crystals and the fcc-Co magnetic crystal layer is not measured, if a temperature of heat treatment is 800°C in the reducing step. In contrast, it was confirmed that a mixed structure between the Sm_2Co_{17} magnetic crystals and the fcc-Co magnetic crystal layer is easily measured, if a temperature of heat treatment is 600°C, 700°C and 750°C in the reducing step.

[0116] FIGS. 28 is a graph showing a change in properties according to a temperature of heat treatment in a rare-earth oxide.

[0117] Referring to FIG. 28, an Sm_2O_3 rare-earth oxide was heat-treated under a hydrogen atmosphere at a heating rate of 10°C/min from 25°C to 1000°C, after which a weight loss (%) of the heat-treated rare-earth oxide was measured and shown. As can be understood from FIG. 28, it was confirmed that the rare-earth oxide has almost no weight loss even when heat-treated at 1000°C, and thus reduction does not easily occur.

[0118] FIGS. 29 to 31 are pictures and graphs showing a comparison of diameters of hybrid magnetic fibers according to Examples 1 and 3 of the present invention.

[0119] Referring to FIG. 29, an SEM picture was taken of the hybrid magnetic fiber according to above Example 3 and shown in (a) of FIG. 29 and a diameter of the hybrid magnetic fiber was measured and shown in (b) of FIG. 29. As can be understood from (a) and (b) of FIG. 29, it was confirmed that the hybrid magnetic fiber according to above Example 3 has a diameter of 250 nm or less and has a chain structure.

[0120] Referring to FIGS. 30 and 31, an SEM picture was taken of the hybrid magnetic fibers according to above Example 1 having a diameter of about 500 nm and a diameter of about 1000 nm and shown in (a) of FIG. 30 and (a) of FIG. 31, respectively, and a diameter of each hybrid magnetic fiber was measured and shown in (b) of FIG. 30 and (b) of FIG. 31. As can be understood from FIGS. 30 and 31, it was confirmed that the hybrid magnetic fibers according to above Example 1 having a diameter of about 500 nm and a diameter of about 1000 nm have a structure of magnetic crystal-magnetic boundary layer.

[0121] Although the present invention has been described in detail with reference to exemplary embodiments, the scope of the present invention is not limited to a specific embodiment and should be interpreted by the attached claims. In addition, those skilled in the art should understand that many modifications and variations are possible without departing from the scope of the present invention.

[Industrial Applicability]

[0122] According to an embodiment of the present invention, a hybrid magnetic fiber may be used in various fields of industry such as permanent magnet, an electric motor, a micro relay, a sensor, etc.

Claims

1. A method for preparing a hybrid magnetic fiber, the method comprising:

providing a source solution including a first source material containing a rare-earth element and a second source material containing a transition-metal element;
electrospinning the source solution to form a preliminary hybrid magnetic fiber including a rare-earth oxide and a transition-metal oxide; and
reducing the preliminary hybrid magnetic fiber to form a hybrid magnetic fiber including magnetic crystals containing a compound of the rare-earth element and the transition-metal element, and a magnetic boundary layer including the transition-metal element.

2. The method of claim 1, wherein the magnetic crystal has a hard-magnetic property, and the magnetic boundary layer has a soft-magnetic property.

3. The method of claim 1, wherein the magnetic boundary layer follows a magnetization behavior of the magnetic crystal.

4. The method of claim 1, wherein a molar fraction of the rare-earth element in the source solution is more than 9.290 at% and less than 10.562 at%.

5. The method of claim 1, wherein the forming of the hybrid magnetic fiber comprises:

mixing the preliminary hybrid magnetic fiber with a reducing agent;
heat-treating the preliminary hybrid magnetic fiber mixed with the reducing agent; and

washing the heat-treated preliminary hybrid magnetic fiber with a cleaning solution.

6. The method of claim 5, wherein the preliminary hybrid magnetic fiber mixed with the reducing agent is heat-treated at a temperature of more than 500°C and less than 800°C.

7. The method of claim 5, wherein the reducing agent comprises calcium (Ca).

8. The method of claim 5, wherein the cleaning solution comprises at least one of ammonium chloride (NH4Cl) and methanol (CH3OH).

9. The method of claim 1, wherein the source solution further comprises a crystallization source including a metal, and a viscous source including a polymer.

10. The method of claim 1, wherein the rare-earth element comprises one of La, Ce, Pr, Nd, Sm, or Gd.

11. The method of claim 1, wherein the transition-metal element comprises one of Fe, Co, or Ni.

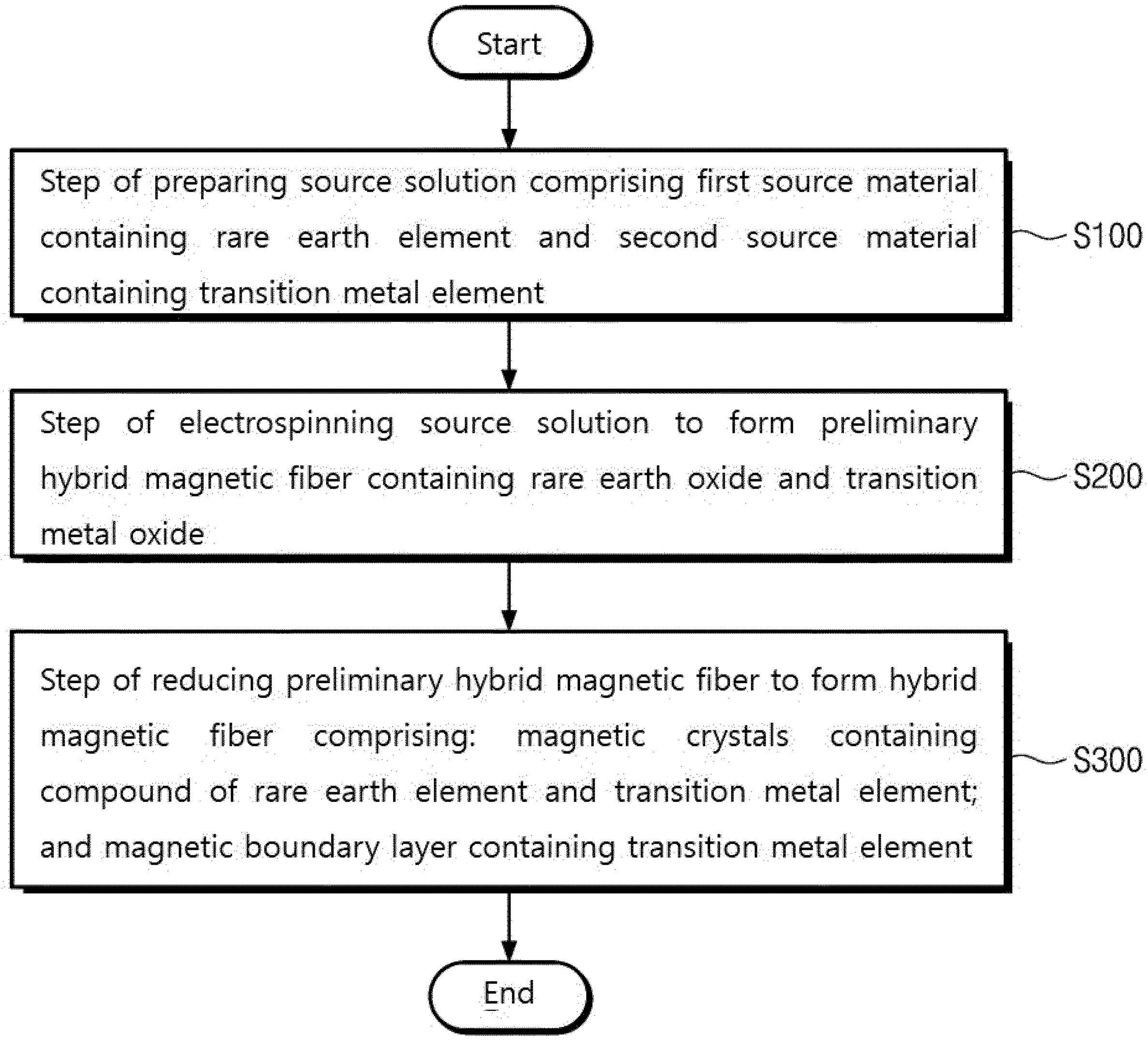
12. A hybrid magnetic fiber comprising:

a plurality of magnetic crystals including a compound of a rare-earth element and a transition-metal element; and
a magnetic boundary layer disposed between the magnetic crystals adjacent to each other, surrounding the magnetic crystals, and including the transition-metal element.

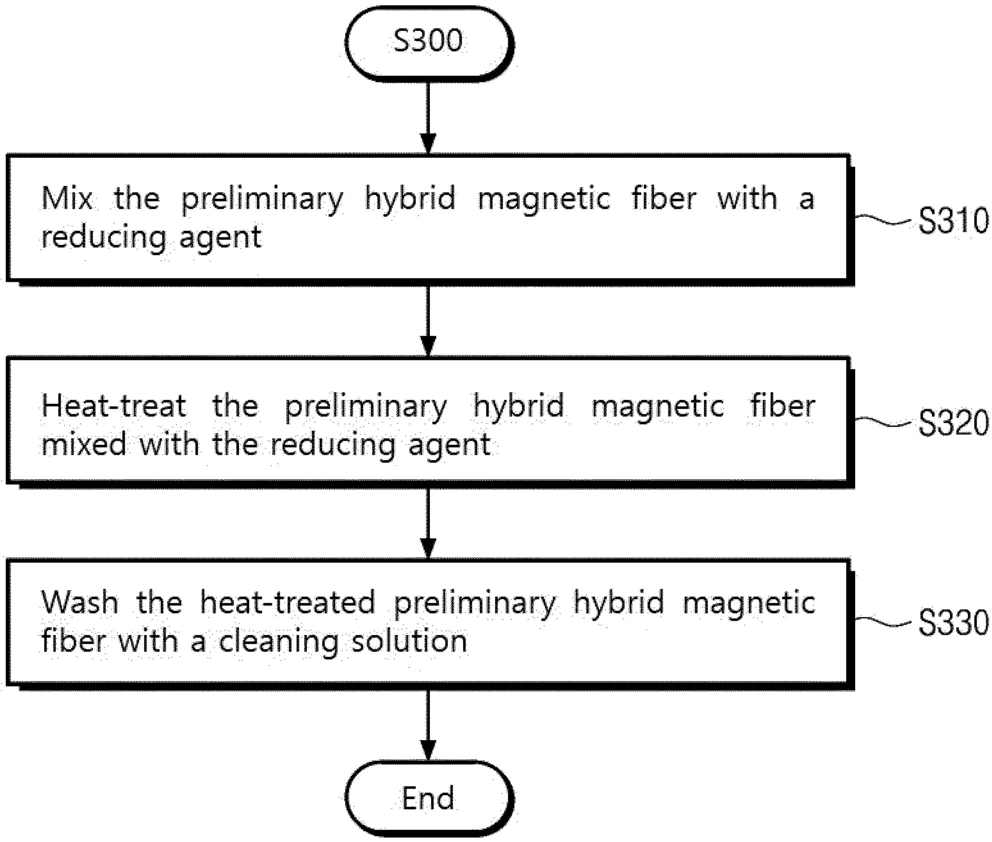
13. The hybrid magnetic fiber of claim 12, wherein a volume fraction of the magnetic boundary layer is greater than 0 vol% and less than 10 vol% in the hybrid magnetic fiber.

14. The hybrid magnetic fiber of claim 12, wherein the magnetic crystal has a hard-magnetic property, and the magnetic boundary layer has a soft-magnetic property, in which the magnetic boundary layer follows a magnetization behavior of the magnetic crystal.

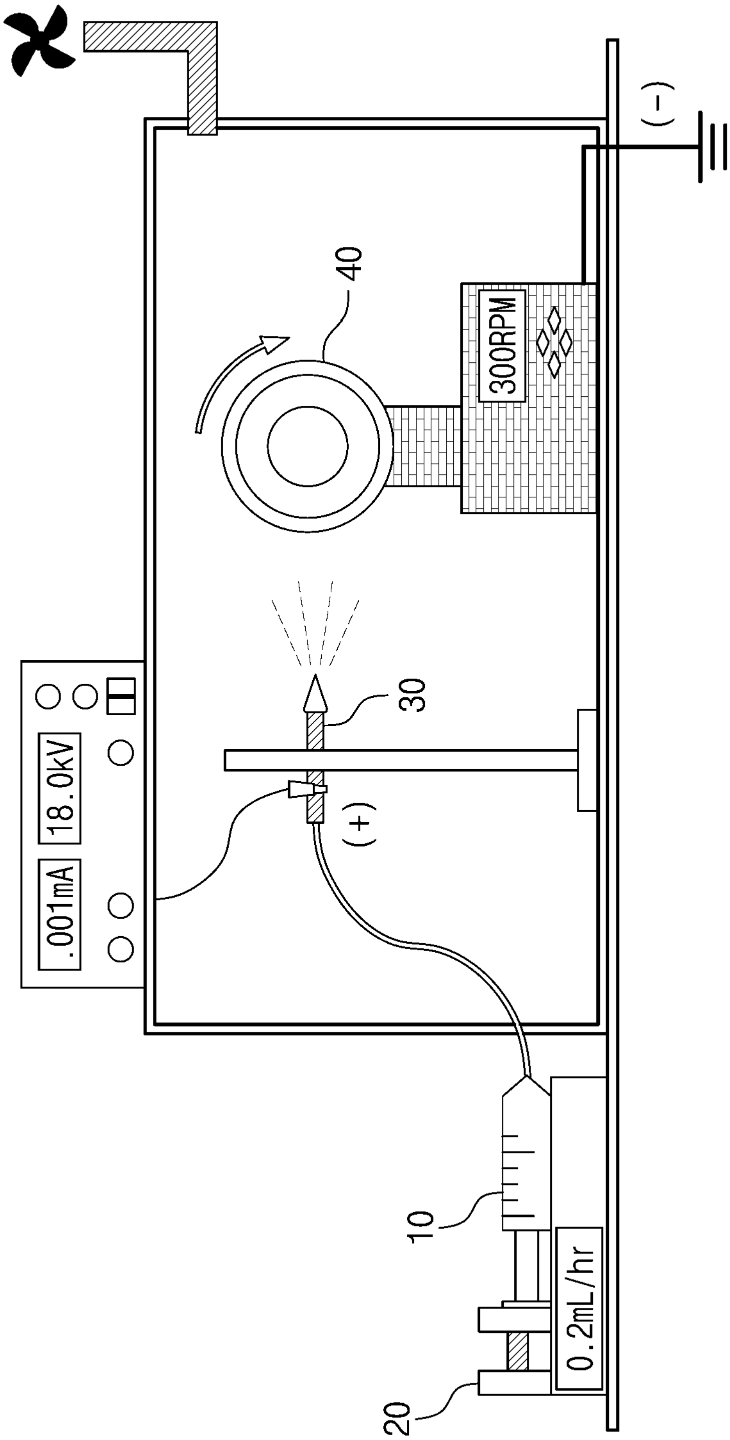
【Fig. 1】


Start
Step of preparing source solution comprising first source material containing rare earth element and second source material containing transition metal element
S100
Step of electrospinning source solution to form preliminary hybrid magnetic fiber containing rare earth oxide and transition metal oxide
S200
Step of reducing preliminary hybrid magnetic fiber to form hybrid magnetic fiber comprising: magnetic crystals containing compound of rare earth element and transition metal element; and magnetic boundary layer containing transition metal element
S300
End

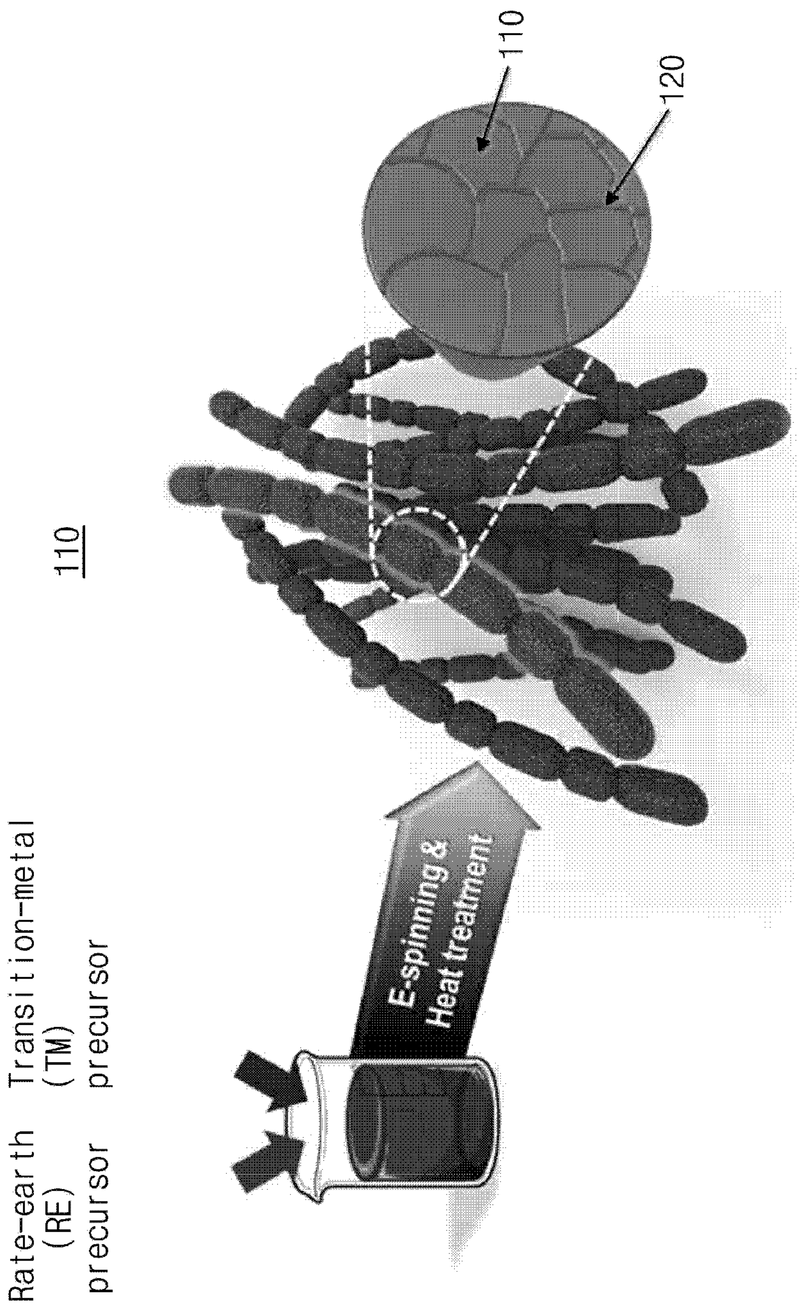
【Fig. 2】


S300
Mix the preliminary hybrid magnetic fiber with a reducing agent
S310
Heat-treat the preliminary hybrid magnetic fiber mixed with the reducing agent
S320
Wash the heat-treated preliminary hybrid magnetic fiber with a cleaning solution
S330
End

【Fig. 3】

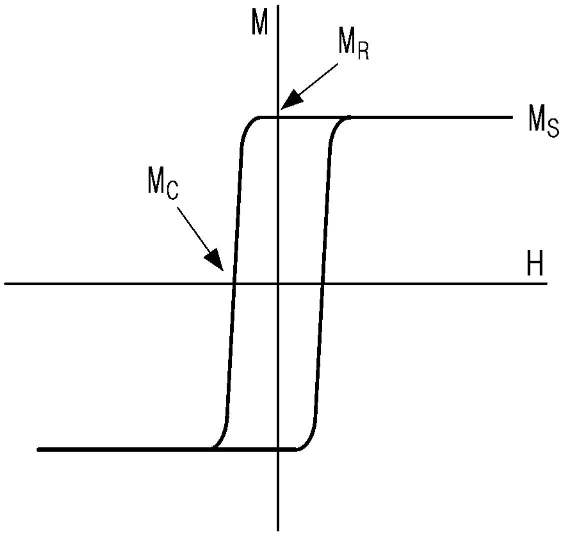


【Fig. 4】

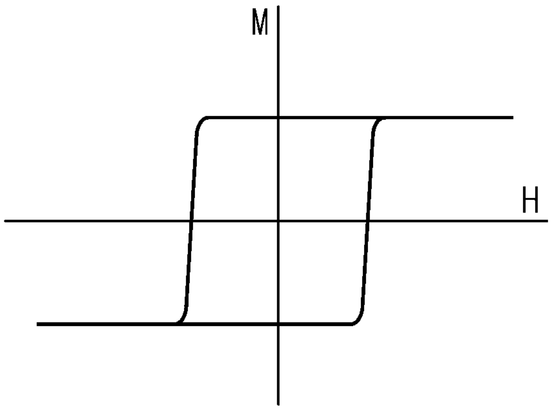

Rate-earth (RE) precursor
Transition-metal (TM) precursor
E-spinning & Heat treatment
110
110
120

【Fig. 5】

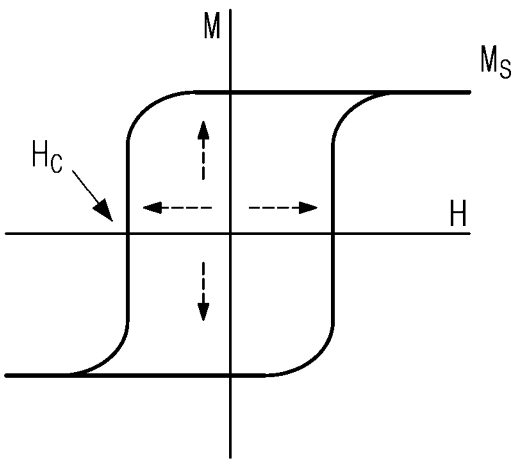
(a)



(b)

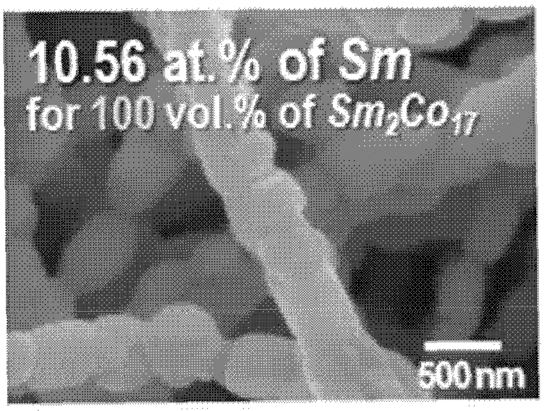


【Fig. 6】

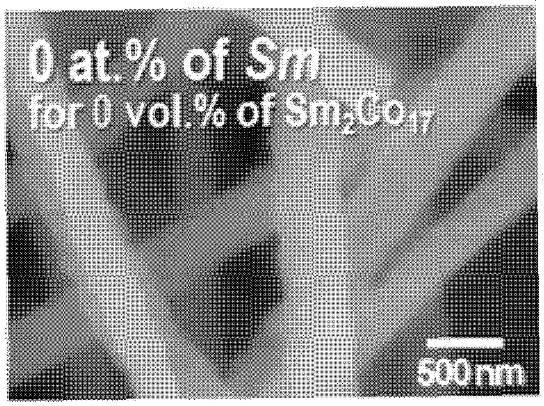


【Fig. 7】

(a)

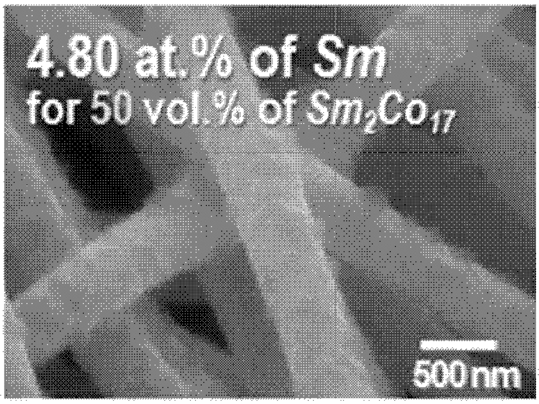

10.56 at.% of Sm
for 100 vol.% of Sm2Co17
500 nm

(b)

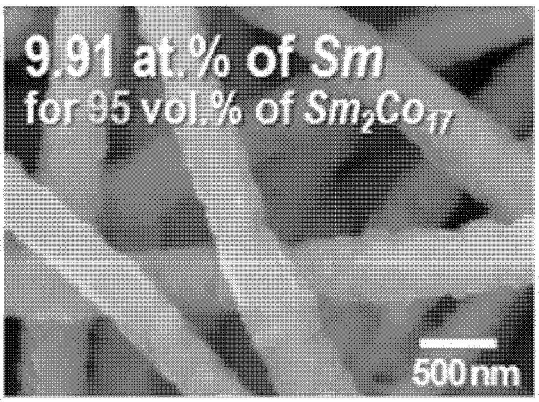

0 at.% of Sm
for 0 vol.% of Sm2Co17
500 nm

【Fig. 8】

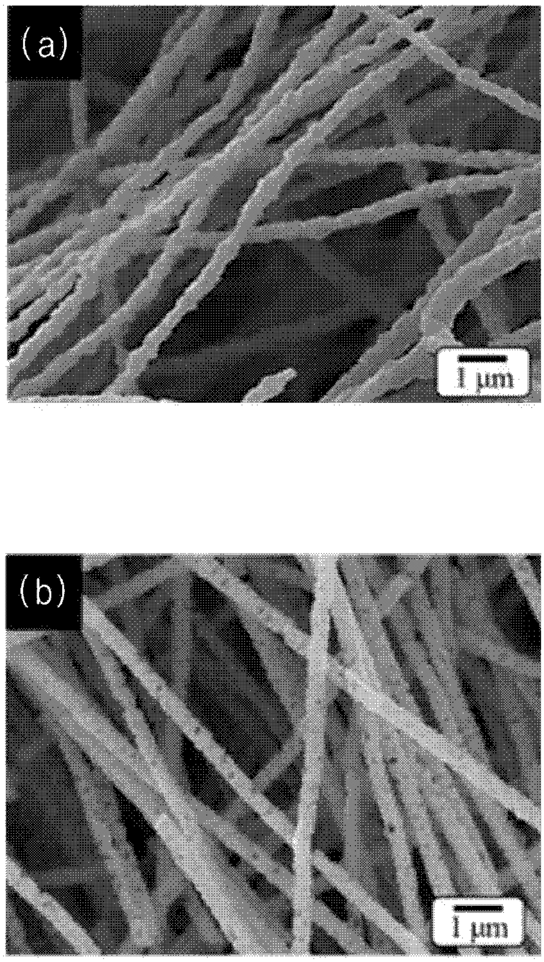
(a)


4.80 at.% of Sm
for 50 vol.% of Sm2Co17
500 nm

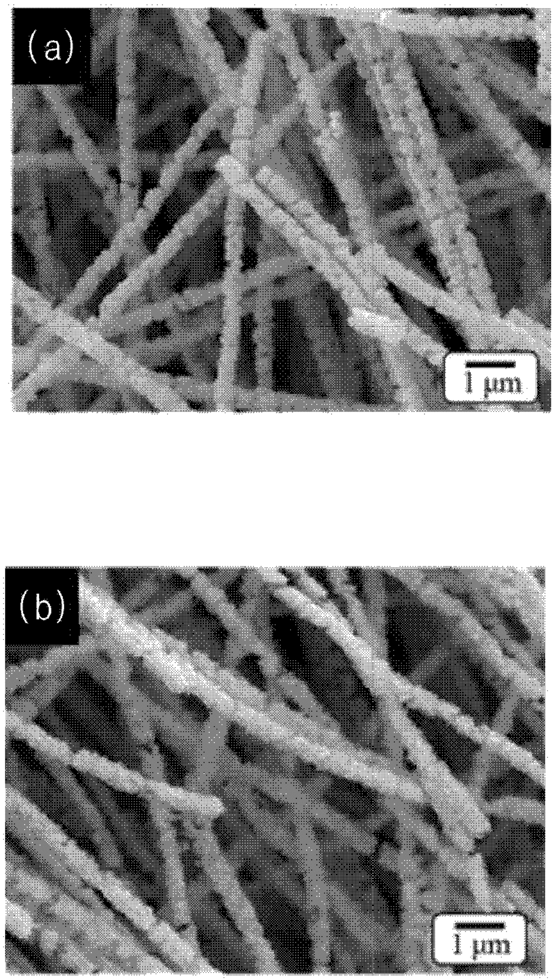
(b)


9.91 at.% of Sm
for 95 vol.% of Sm2Co17
500 nm

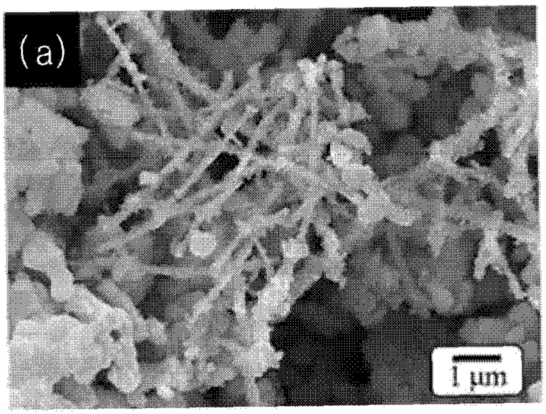
【Fig. 9】

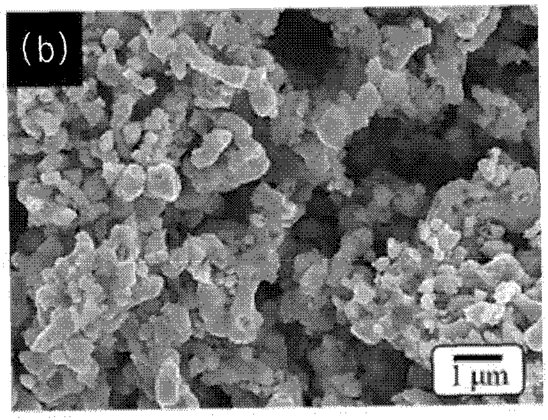


【Fig. 10】

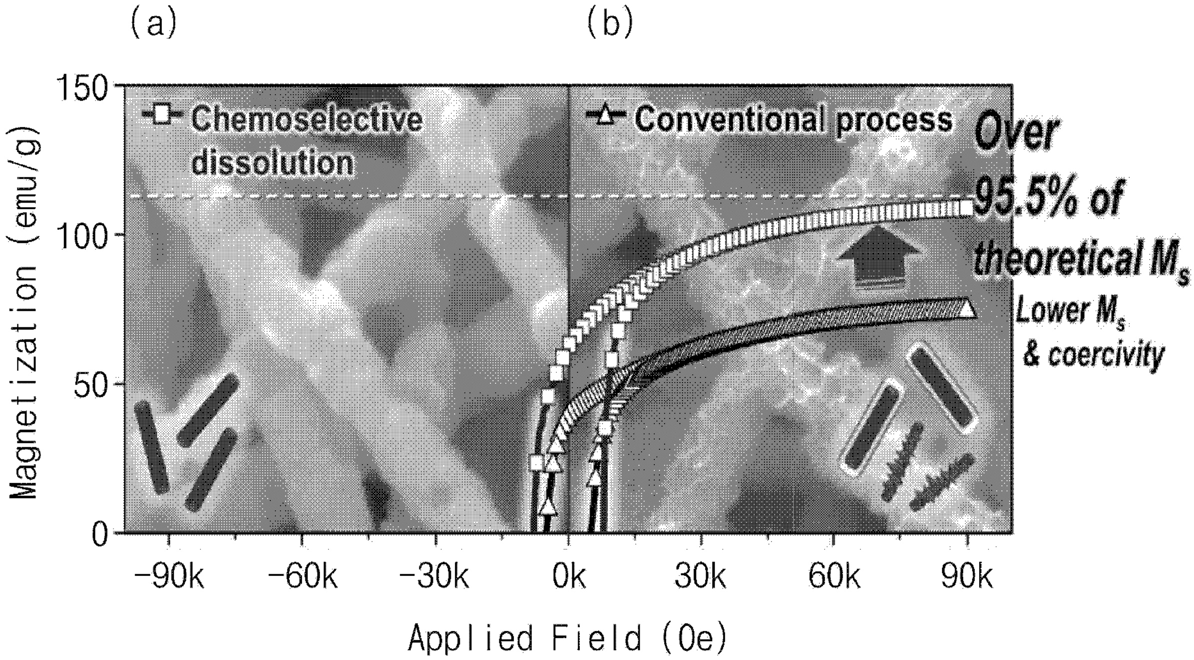


【Fig. 11】

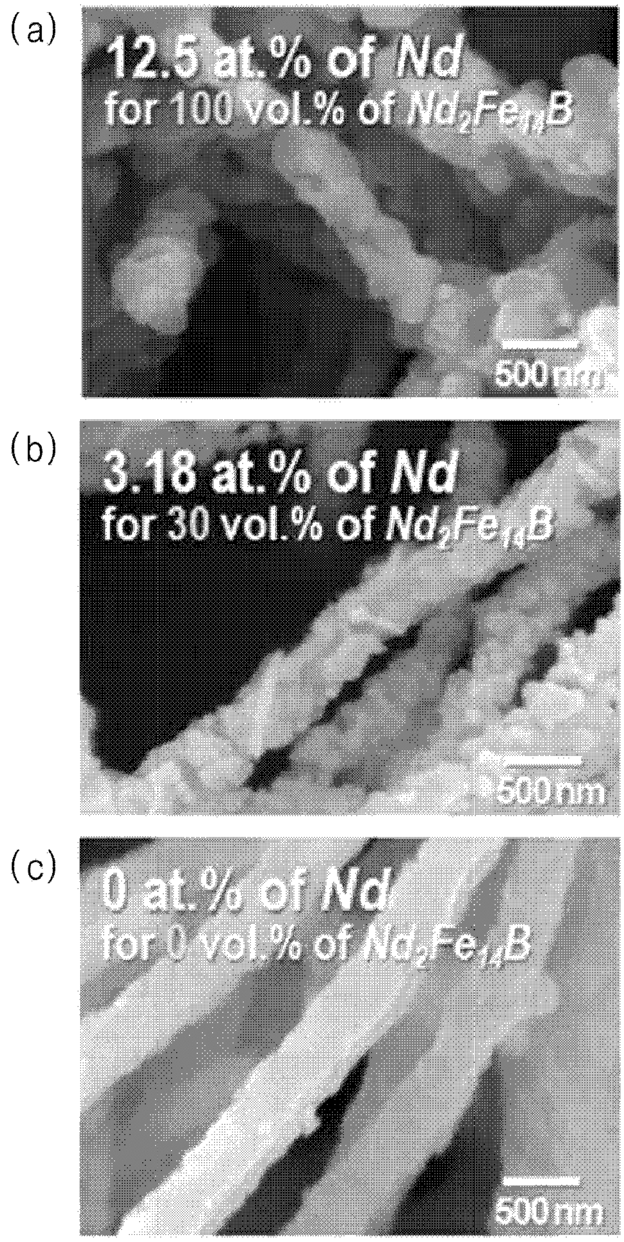




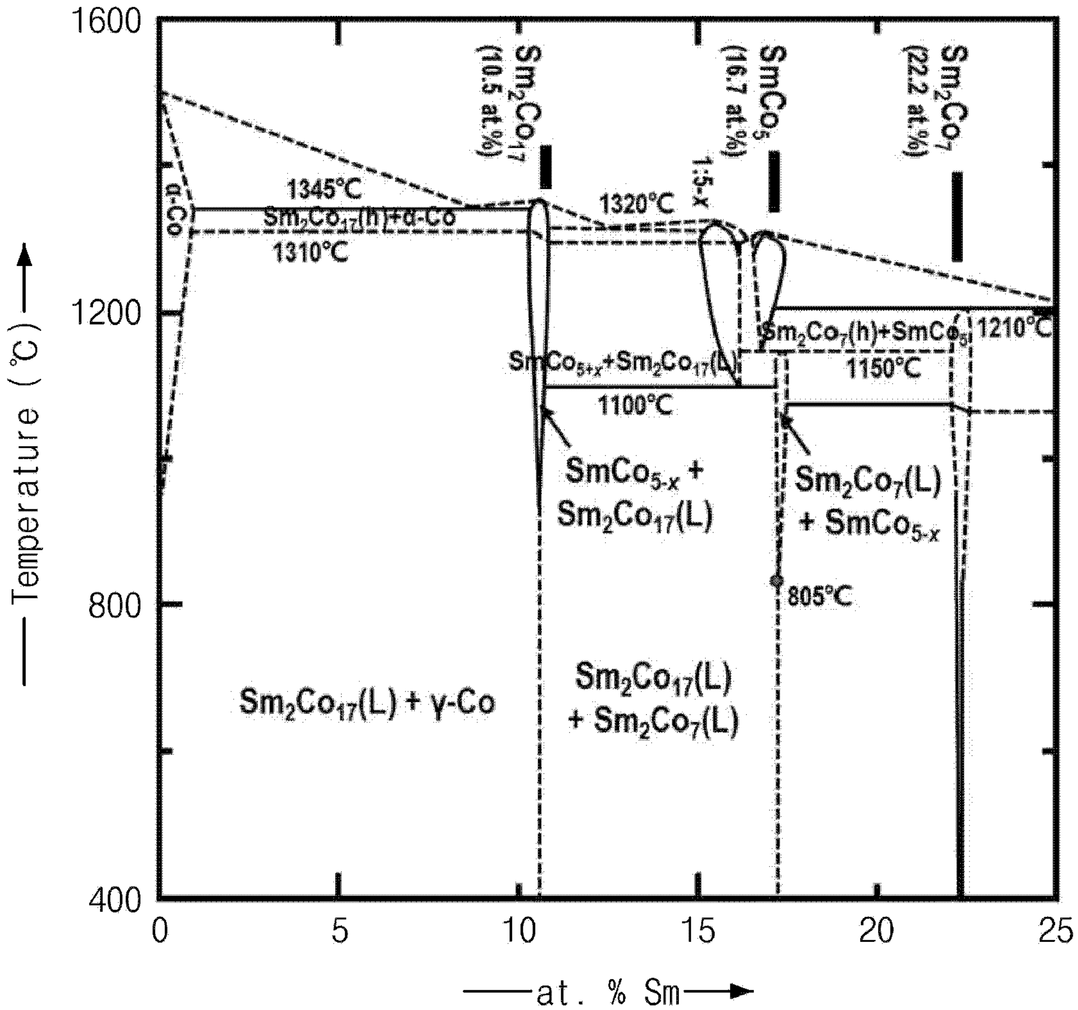
【Fig. 12】


(a)
(b)
Chemoselective dissolution
Conventional process
Over 95.5% of theoretical M_s
Lower M_s & coercivity
Magnetization (emu/g)
150
100
50
0
-90k
-60k
-30k
0k
30k
60k
90k
Applied Field (Oe)

【Fig. 13】

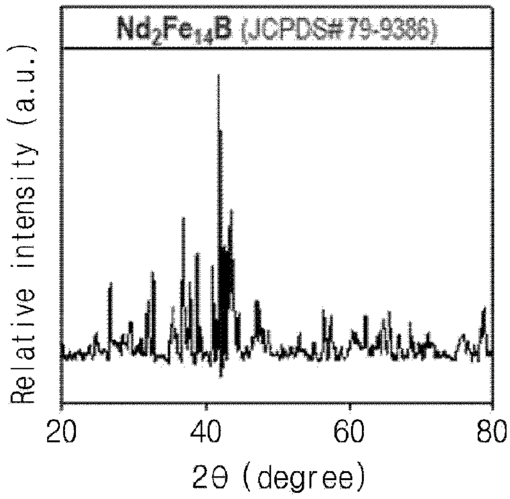

(a)
12.5 at.% of Nd
for 100 vol.% of Nd2Fe14B
500 nm
(b)
3.18 at.% of Nd
for 30 vol.% of Nd2Fe14B
500 nm
(c)
0 at.% of Nd
for 0 vol.% of Nd2Fe14B
500 nm

【Fig. 14】

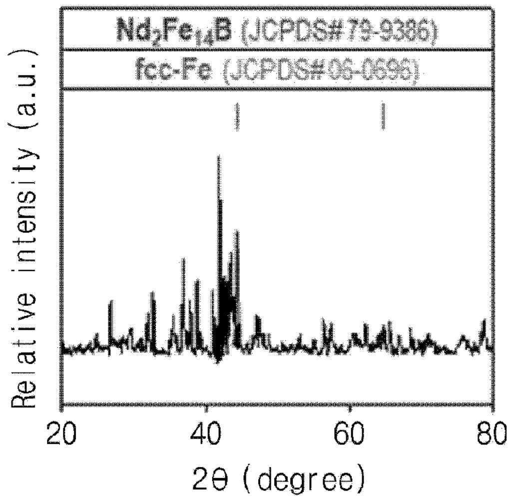

1600
1200
800
400
0
5
10
15
20
25
Temperature (℃)
at. % Sm
Sm2Co17 (10.5 at.%)
SmCo5 (16.7 at.%)
Sm2Co7 (22.2 at.%)
α-Co
1345°C
Sm2Co17(h)+α-Co
1310°C
1320°C
1:5-x
Sm2Co7(h)+SmCo5
1210°C
SmCo5+x+Sm2Co17(L)
1150°C
1100°C
SmCo5-x + Sm2Co17(L)
Sm2Co7(L) + SmCo5-x
805°C
Sm2Co17(L) + γ-Co
Sm2Co17(L) + Sm2Co7(L)

【Fig. 15】

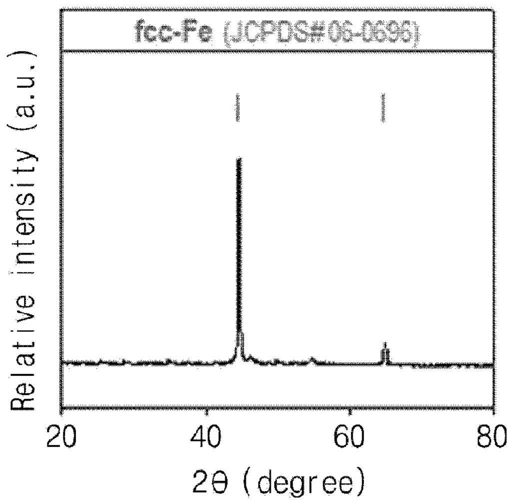
(a)


$Nd_2Fe_{14}B$ (JCPDS#79-9386)
Relative intensity (a.u.)
20
40
60
80
2θ (degree)

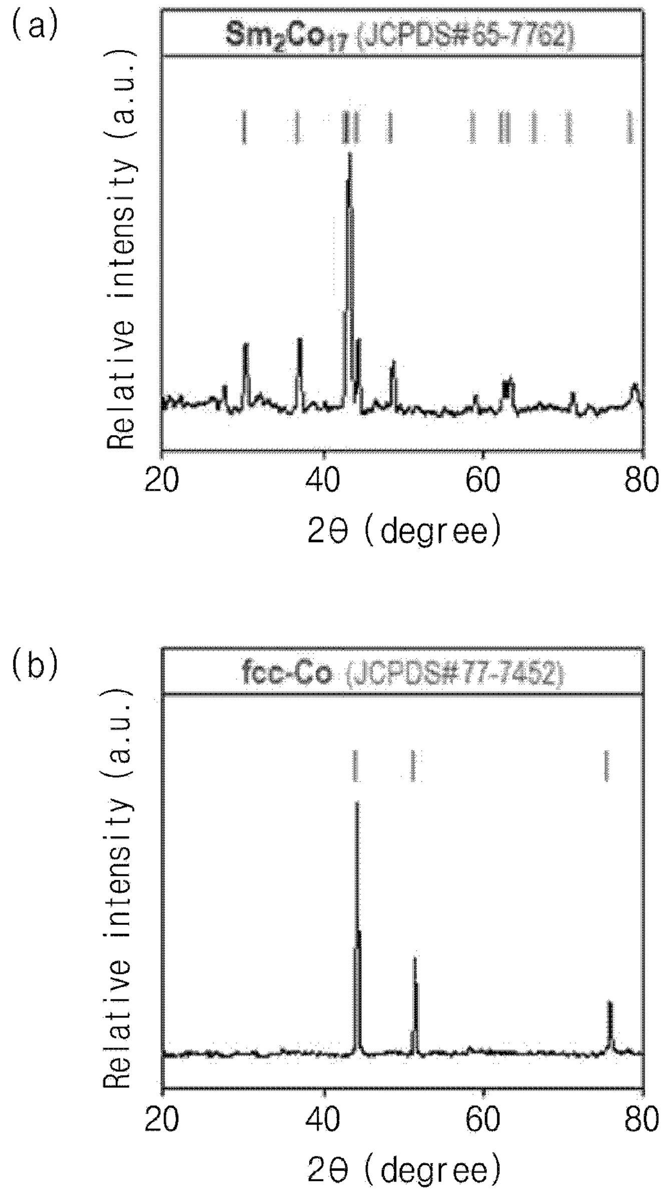
(b)


$Nd_2Fe_{14}B$ (JCPDS#79-9386)
fcc-Fe (JCPDS#06-0696)
Relative intensity (a.u.)
20
40
60
80
2θ (degree)

(c)

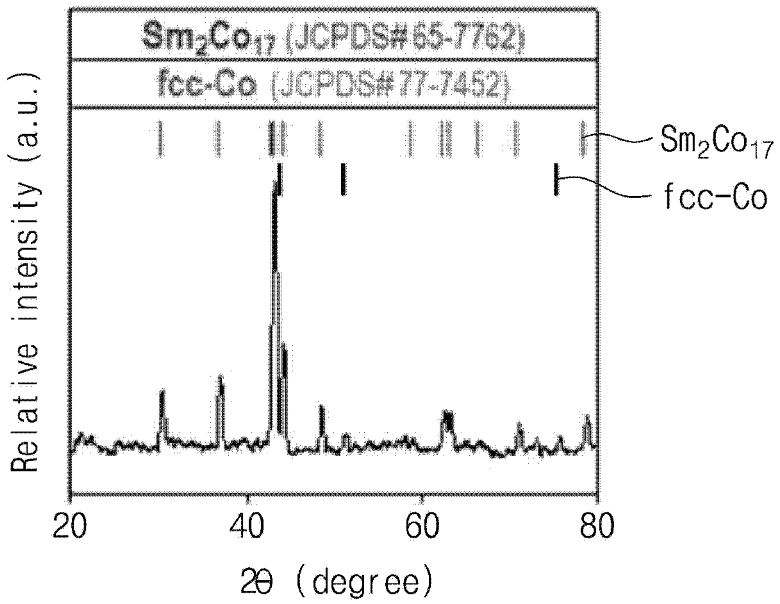

fcc-Fe (JCPDS#06-0696)
Relative intensity (a.u.)
20
40
60
80
2θ (degree)

【Fig. 16】

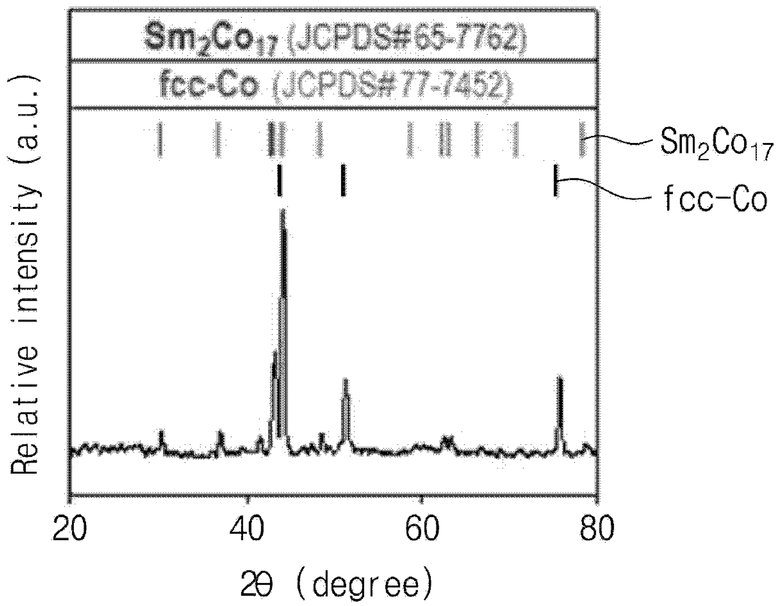

(a)
Sm2Co17 (JCPDS#65-7762)
Relative intensity (a.u.)
20
40
60
80
2θ (degree)
(b)
fcc-Co (JCPDS#77-7452)
Relative intensity (a.u.)
20
40
60
80
2θ (degree)

【Fig. 17】

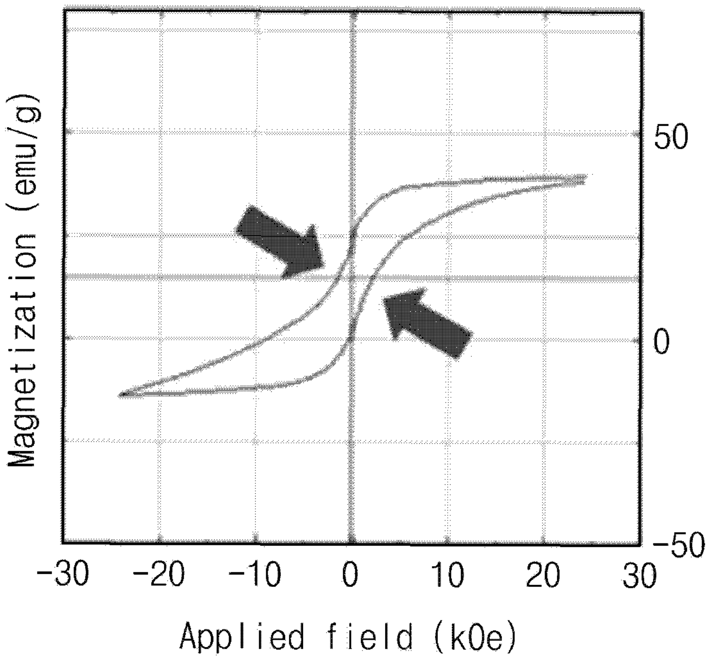
(a)


Sm2Co17 (JCPDS#65-7762)
fcc-Co (JCPDS#77-7452)
Sm2Co17
fcc-Co
Relative intensity (a.u.)
20
40
60
80
2θ (degree)

(b)

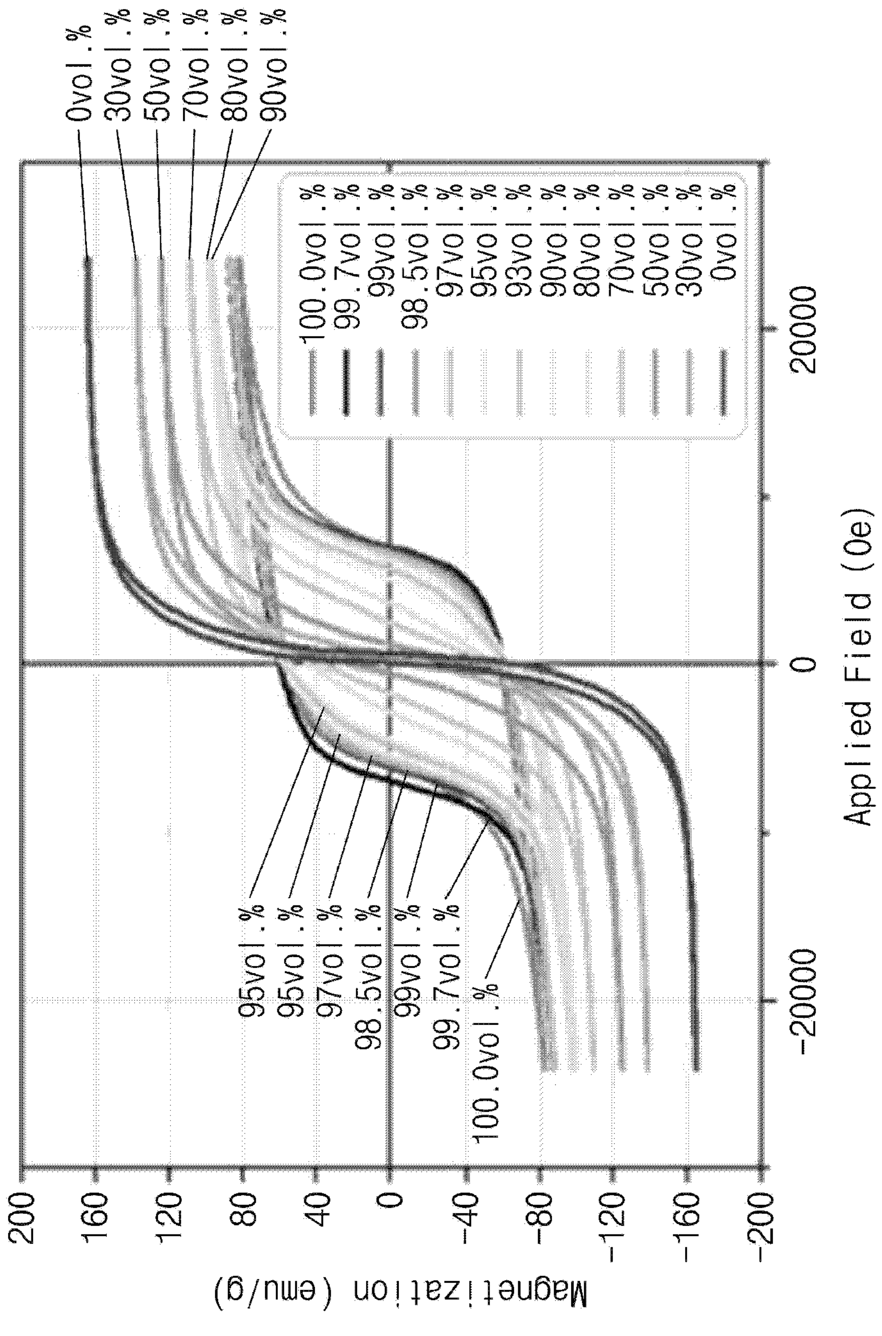

Sm2Co17 (JCPDS#65-7762)
fcc-Co (JCPDS#77-7452)
Sm2Co17
fcc-Co
Relative intensity (a.u.)
20
40
60
80
2θ (degree)

【Fig. 18】

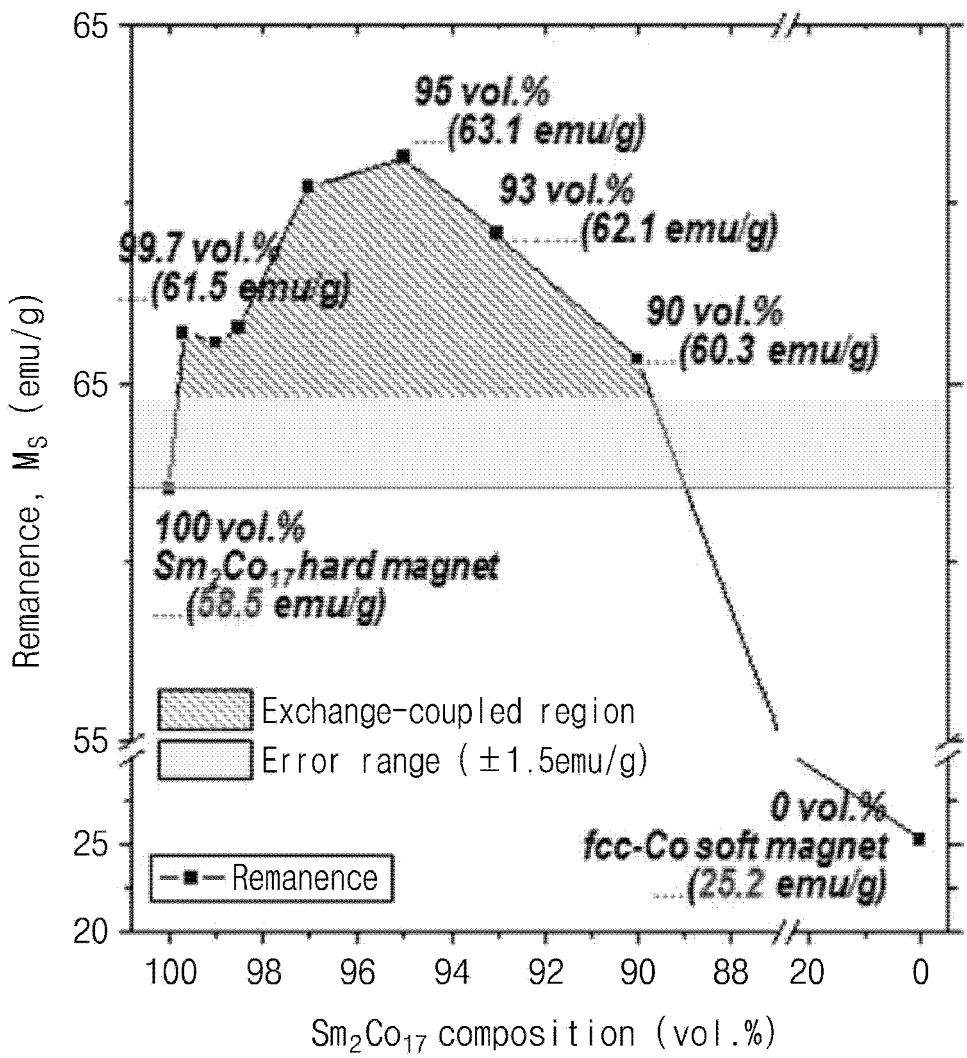


Sm_2Co_{17}:fcc-Co=50:50 (vol.%)

【Fig. 19】

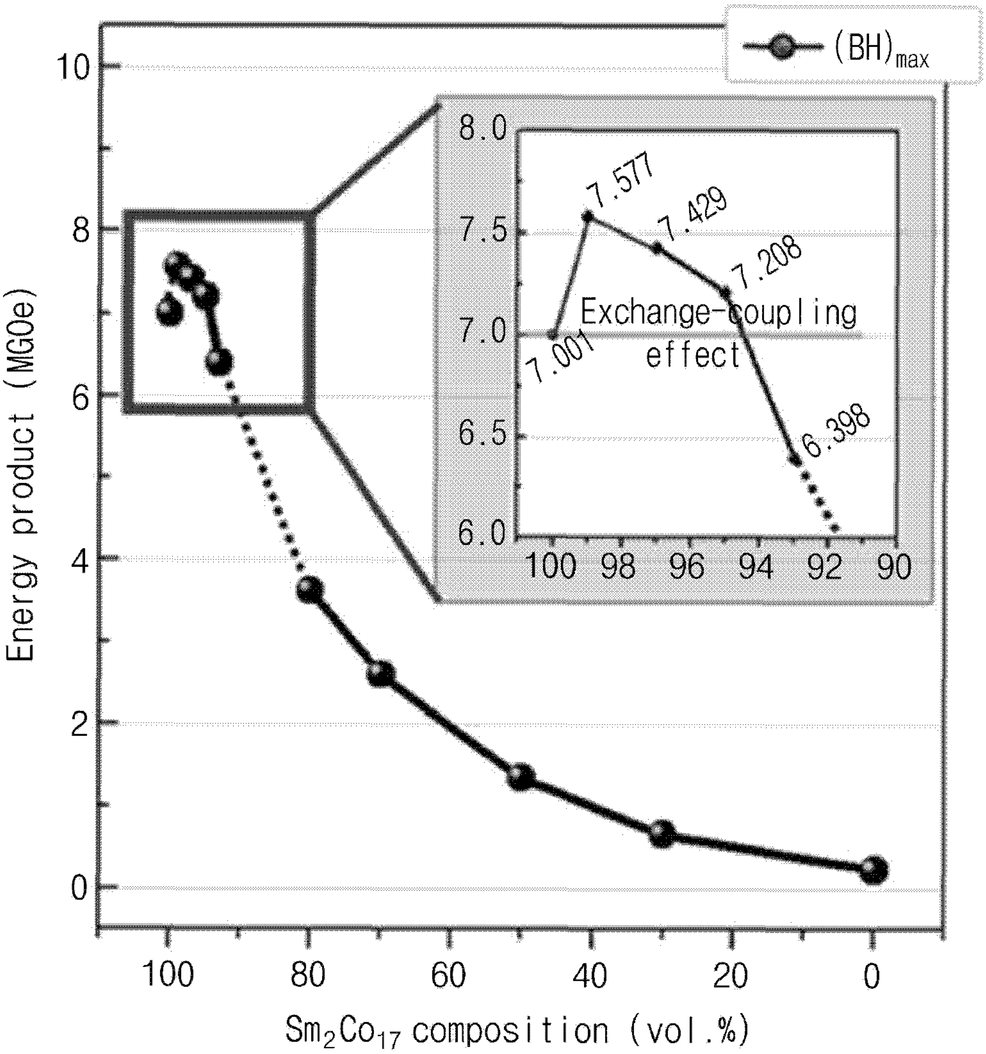

Magnetization (emu/g)
Applied Field (Oe)
200
160
120
80
40
0
-40
-80
-120
-160
-200
-20000
0
20000
0vol.%
30vol.%
50vol.%
70vol.%
80vol.%
90vol.%
95vol.%
95vol.%
97vol.%
98.5vol.%
99vol.%
99.7vol.%
100.0vol.%
100.0vol.%
99.7vol.%
99vol.%
98.5vol.%
97vol.%
95vol.%
93vol.%
90vol.%
80vol.%
70vol.%
50vol.%
30vol.%
0vol.%

【Fig. 20】

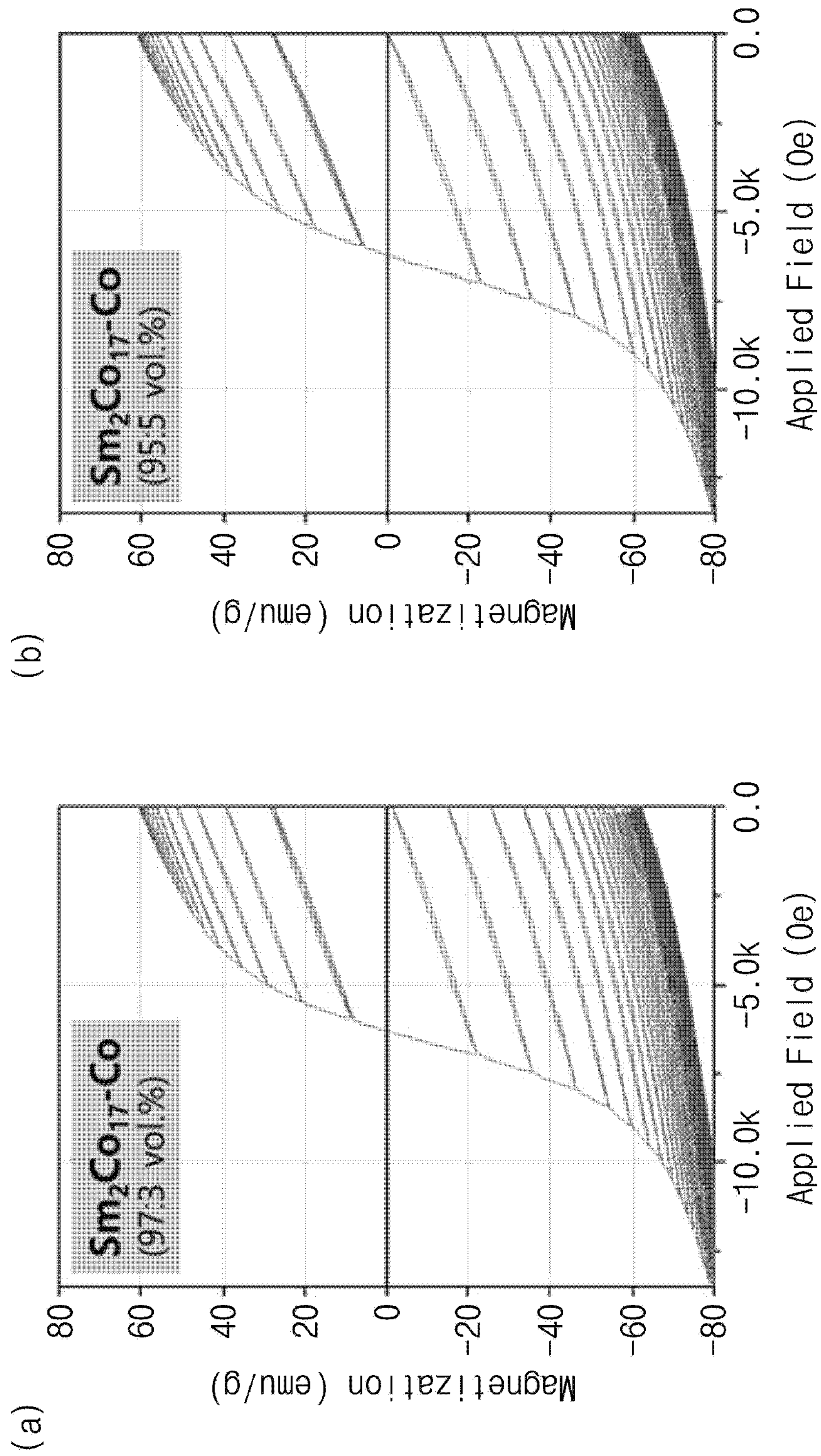


95 vol.%
(63.1 emu/g)
93 vol.%
(62.1 emu/g)
99.7 vol.%
(61.5 emu/g)
90 vol.%
(60.3 emu/g)
100 vol.%
Sm2Co17 hard magnet
(58.5 emu/g)
Exchange-coupled region
Error range (±1.5emu/g)
Remanence
0 vol.%
fcc-Co soft magnet
(25.2 emu/g)
Remanence, MS (emu/g)
Sm2Co17 composition (vol.%)
65
65
55
25
20
100
98
96
94
92
90
88
20
0

【Fig. 21】

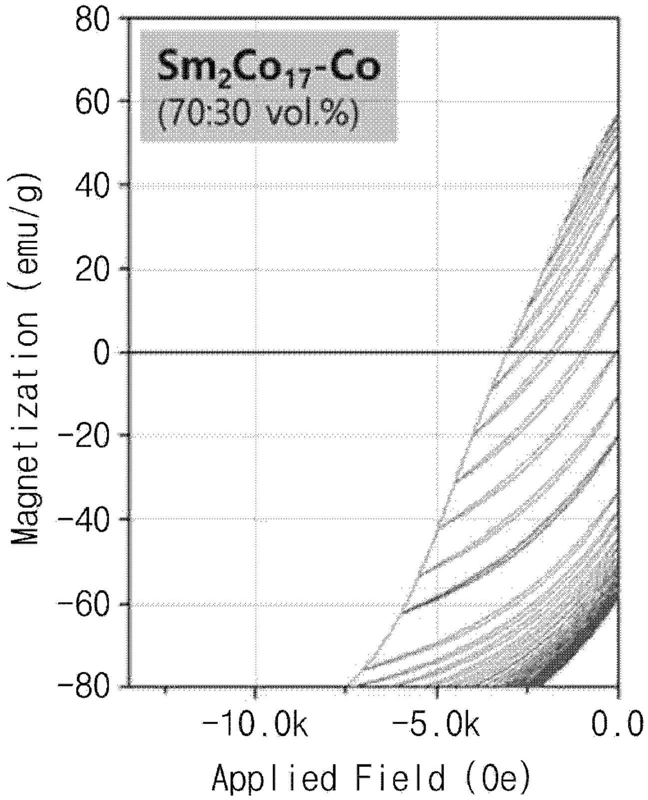

(BH)max
10
8
6
4
2
0
Energy product (MGOe)
100
80
60
40
20
0
Sm2Co17 composition (vol.%)
8.0
7.5
7.0
6.5
6.0
100
98
96
94
92
90
7.577
7.429
7.208
7.001
6.398
Exchange-coupling
effect

【Fig. 22】

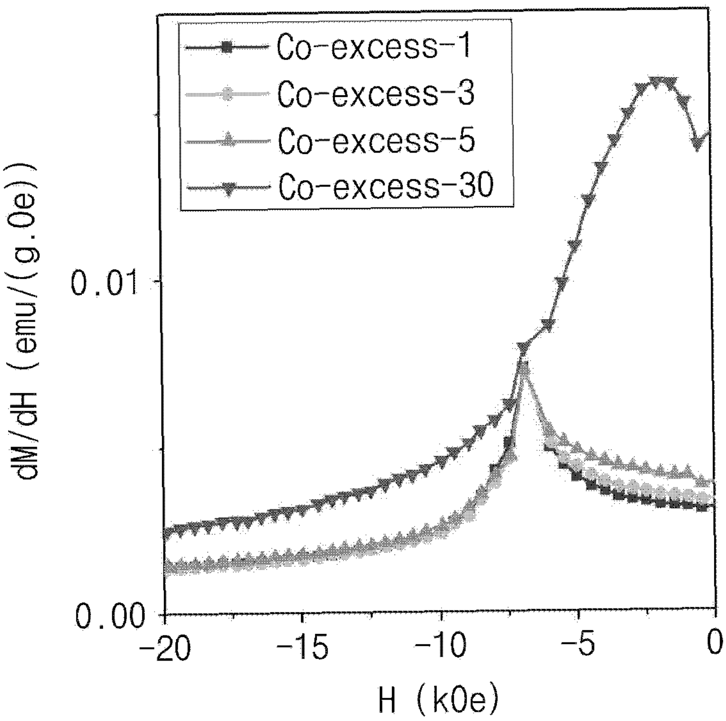


(a)
Sm_2Co_{17}-Co
(97:3 vol.%)
Magnetization (emu/g)
Applied Field (Oe)
80
60
40
20
0
-20
-40
-60
-80
-10.0k
-5.0k
0.0
(b)
Sm_2Co_{17}-Co
(95:5 vol.%)
Magnetization (emu/g)
Applied Field (Oe)
80
60
40
20
0
-20
-40
-60
-80
-10.0k
-5.0k
0.0

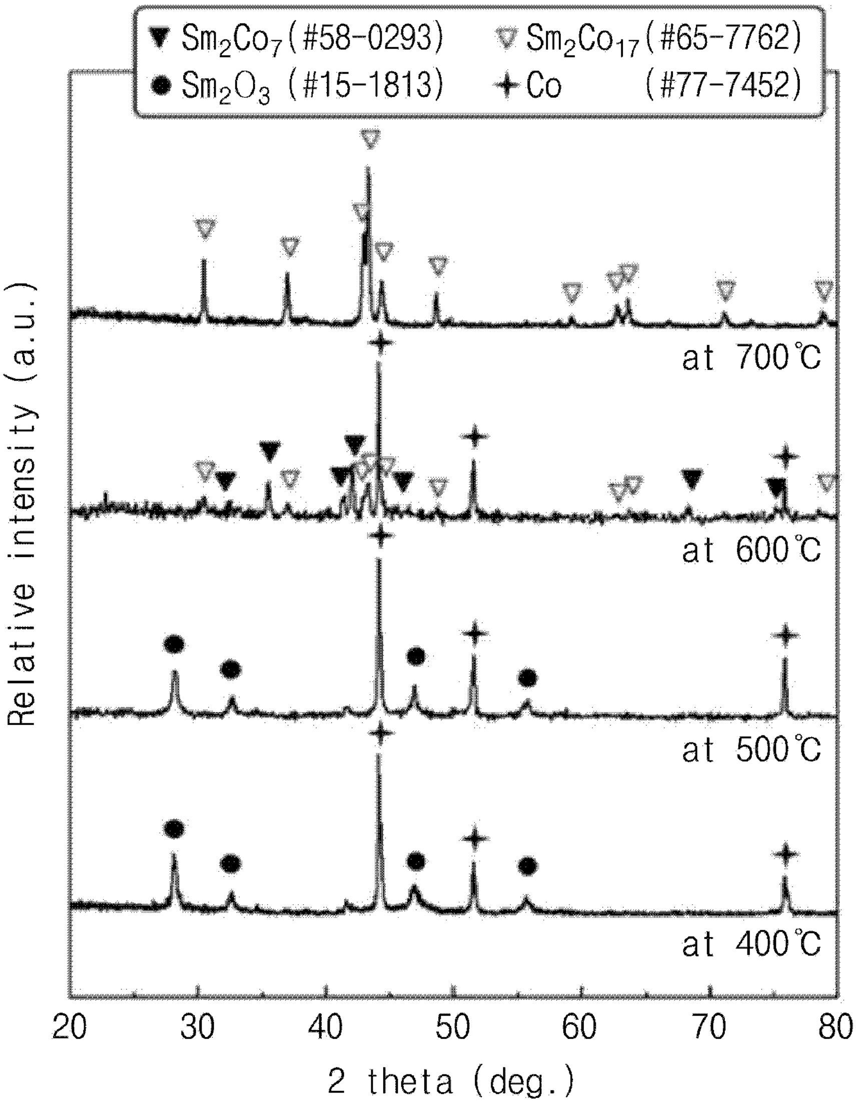
【Fig. 23】


Sm_2Co_{17}-Co
(70:30 vol.%)
Magnetization (emu/g)
80
60
40
20
0
−20
−40
−60
−80
−10.0k
−5.0k
0.0
Applied Field (Oe)

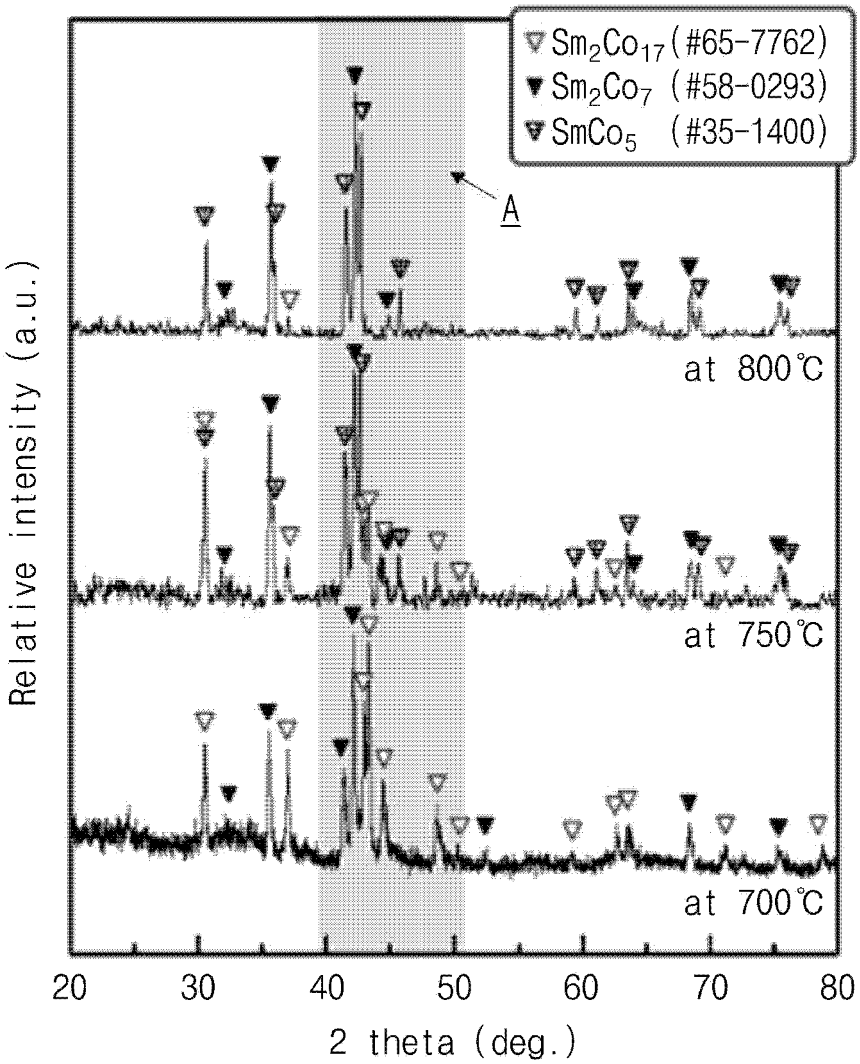
【Fig. 24】


Co-excess-1
Co-excess-3
Co-excess-5
Co-excess-30
dM/dH (emu/(g.Oe))
0.01
0.00
-20
-15
-10
-5
0
H (kOe)

【Fig. 25】

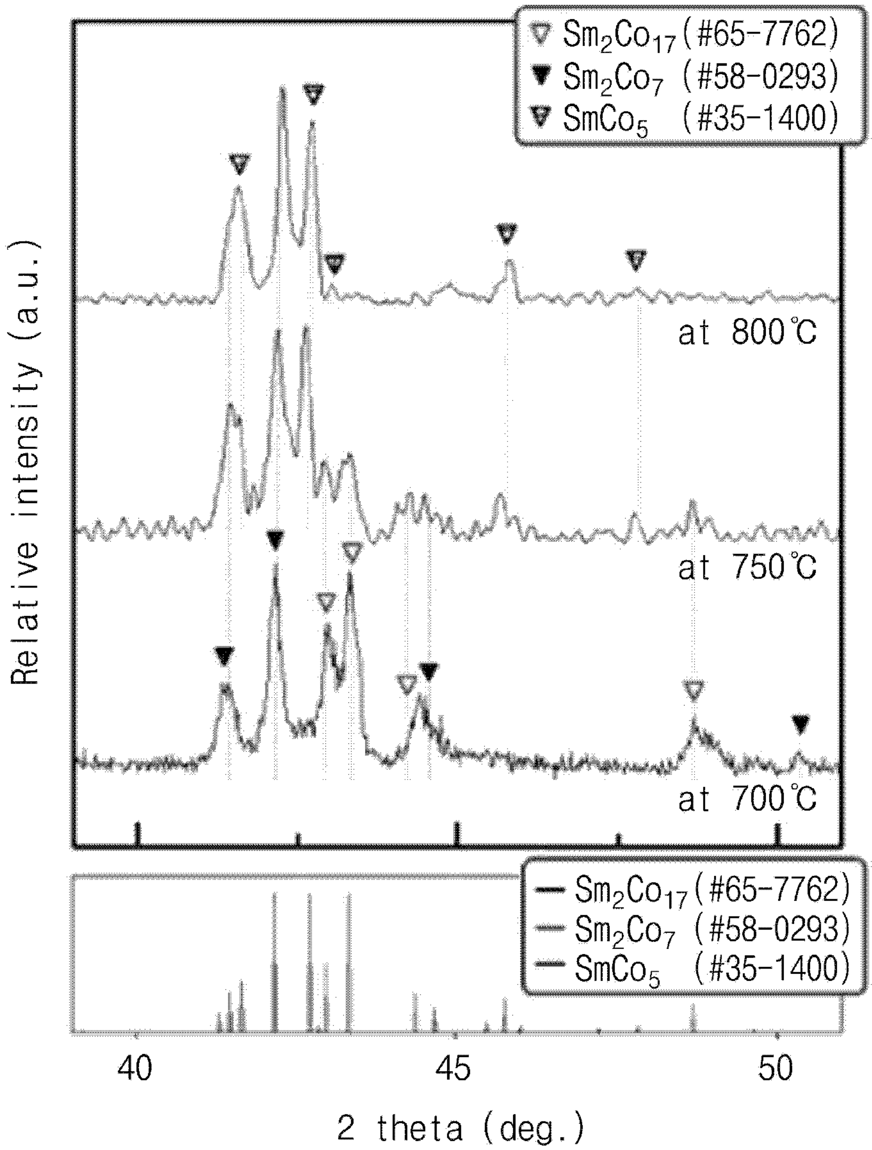

▼ Sm2Co7(#58-0293)
▽ Sm2Co17(#65-7762)
● Sm2O3 (#15-1813)
✦ Co (#77-7452)
at 700℃
at 600℃
at 500℃
at 400℃
Relative intensity (a.u.)
20
30
40
50
60
70
80
2 theta (deg.)

【Fig. 26】

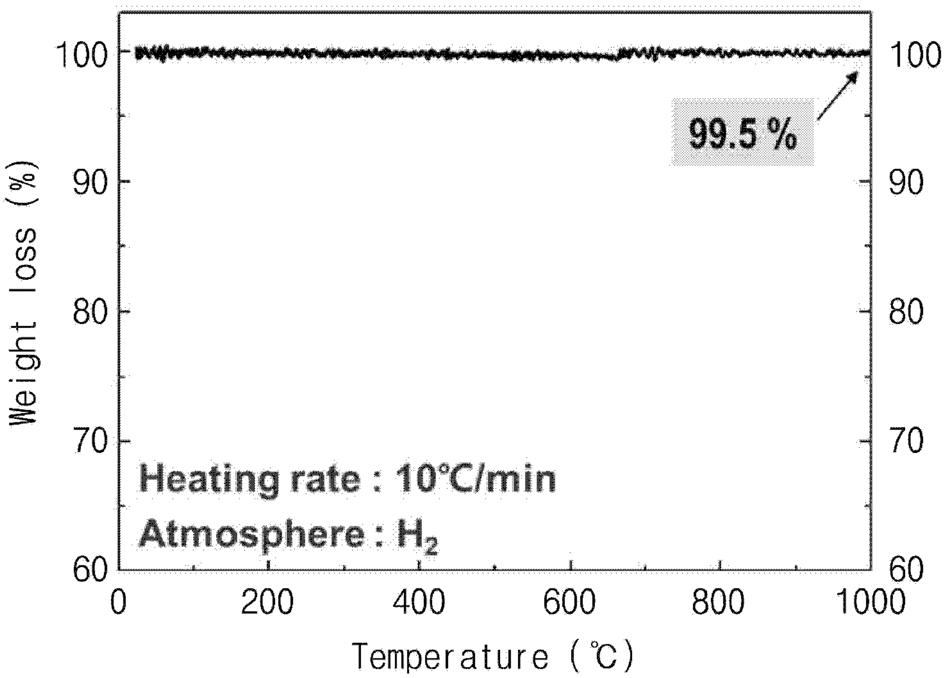


Sm_2Co_{17} (#65-7762)
Sm_2Co_7 (#58-0293)
$SmCo_5$ (#35-1400)
A
at 800℃
at 750℃
at 700℃
Relative intensity (a.u.)
20
30
40
50
60
70
80
2 theta (deg.)

【Fig. 27】

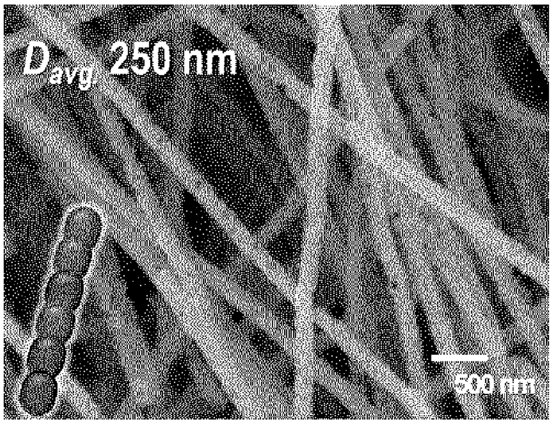

Sm$_2$Co$_{17}$ (#65-7762)
Sm$_2$Co$_7$ (#58-0293)
SmCo$_5$ (#35-1400)
Relative intensity (a.u.)
at 800℃
at 750℃
at 700℃
Sm$_2$Co$_{17}$ (#65-7762)
Sm$_2$Co$_7$ (#58-0293)
SmCo$_5$ (#35-1400)
40
45
50
2 theta (deg.)

【Fig. 28】

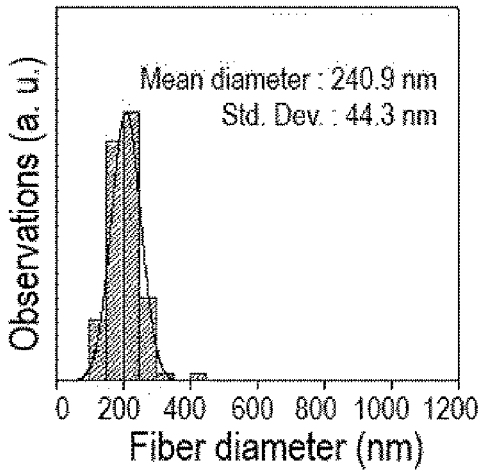

100
90
80
70
60
Weight loss (%)
99.5 %
Heating rate : 10°C/min
Atmosphere : H2
0
200
400
600
800
1000
Temperature (℃)

【Fig. 29】

(a)

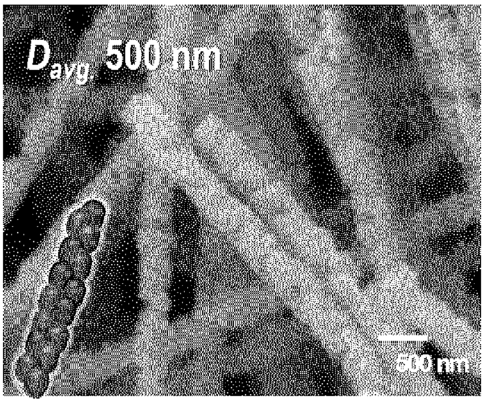

$D_{avg.}$ 250 nm
500 nm

(b)

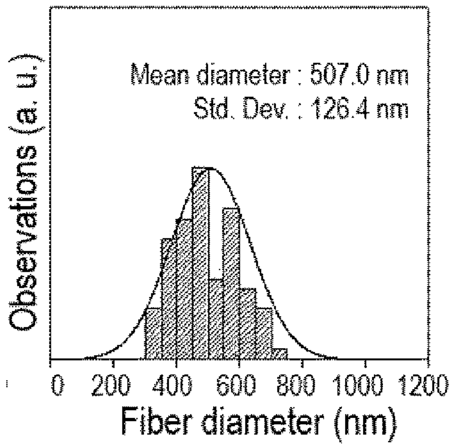

Mean diameter : 240.9 nm
Std. Dev. : 44.3 nm
Observations (a. u.)
0
200
400
600
800
1000
1200
Fiber diameter (nm)

【Fig. 30】

(a)

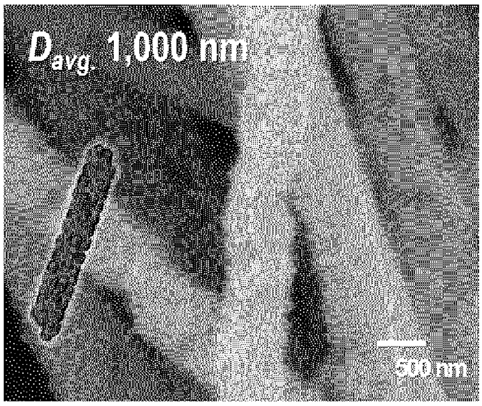

$D_{avg.}$ 500 nm
500 nm

(b)

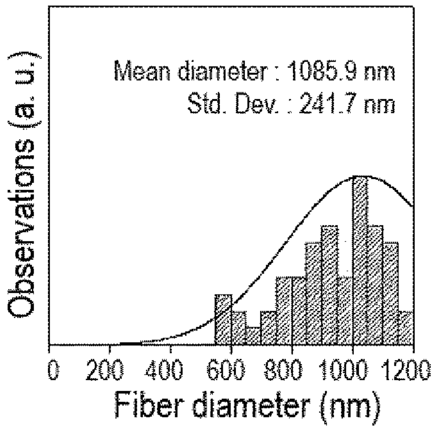

Mean diameter : 507.0 nm
Std. Dev. : 126.4 nm
Observations (a. u.)
0
200
400
600
800
1000
1200
Fiber diameter (nm)

【Fig. 31】

(a)


$D_{avg.}$ 1,000 nm
500 nm

(b)


Mean diameter : 1085.9 nm
Std. Dev. : 241.7 nm
Observations (a. u.)
0
200
400
600
800
1000
1200
Fiber diameter (nm)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2019/001363

A. CLASSIFICATION OF SUBJECT MATTER

H01F 41/02(2006.01)i, H01F 1/055(2006.01)i, H01F 1/14(2006.01)i

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)
H01F 41/02; B22F 3/12; B22F 9/18; B82Y 40/00; C22C 1/04; D04H 1/728; H01F 1/03; H01F 1/053; H01F 1/08; H01F 1/055; H01F 1/14

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models: IPC as above
Japanese utility models and applications for utility models: IPC as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS (KIPO internal) & Keywords: rare earth, transition metal, magnetic fiber, magnetic crystal, magnetic boundary layer

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	KR 10-2017-0104118 A (INDUSTRY-UNIVERSITY COOPERATION FOUNDATION HANYANG UNIVERSITY ERICA CAMPUS) 14 September 2017 See paragraphs [0031]-[0047] and figure 1.	1-14
Y	KR 10-2015-0033528 A (LG ELECTRONICS INC.) 01 April 2015 See paragraph [0051] and figure 1.	1-14
Y	KR 10-2013-0090241 A (LG ELECTRONICS INC. et al.) 13 August 2013 See paragraph [0075] and figure 2.	2,14
A	KR 10-2013-0111036 A (LG ELECTRONICS INC. et al.) 10 October 2013 See paragraphs [0045]-[0054] and figure 1.	1-14
A	KR 10-2012-0043273 A (IUCF-HYU (INDUSTRY-UNIVERSITY COOPERATION FOUNDATION HANYANG UNIVERSITY)) 04 May 2012 See paragraphs [0017]-[0039] and figure 1.	1-14

☐ Further documents are listed in the continuation of Box C. ☒ 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
17 MAY 2019 (17.05.2019)	**17 MAY 2019 (17.05.2019)**

Name and mailing address of the ISA/KR	Authorized officer
Korean Intellectual Property Office Government Complex Daejeon Building 4, 189, Cheongsa-ro, Seo-gu, Daejeon, 35208, Republic of Korea Facsimile No. +82-42-481-8578	Telephone No.

Form PCT/ISA/210 (second sheet) (January 2015)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/KR2019/001363

Patent document cited in search report	Publication date	Patent family member	Publication date
KR 10-2017-0104118 A	14/09/2017	KR 10-1886558 B1	08/08/2018
KR 10-2015-0033528 A	01/04/2015	None	
KR 10-2013-0090241 A	13/08/2013	CN 103890869 A	25/06/2014
		CN 103890869 B	26/09/2017
		KR 10-1778164 B1	13/09/2017
		US 2014-0225024 A1	14/08/2014
		US 9362034 B2	07/06/2016
		WO 2013-115495 A1	08/08/2013
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