(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 3 524 703 A1

# (12) EUROPEAN PATENT APPLICATION

published in accordance with Art. 153(4) EPC

(43) Date of publication:
**14.08.2019 Bulletin 2019/33**

(21) Application number: **17894924.4**

(22) Date of filing: **06.02.2017**

(51) Int Cl.:
***C22C 33/04*** $^{(2006.01)}$ ***C22C 33/00*** $^{(2006.01)}$
***C22C 38/16*** $^{(2006.01)}$

(86) International application number:
**PCT/KR2017/001262**

(87) International publication number:
**WO 2018/143499 (09.08.2018 Gazette 2018/32)**

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR**
Designated Extension States:
**BA ME**
Designated Validation States:
**MA MD**

(71) Applicant: **MTA Co., Ltd.**
**Namyangju-si, Gyeonggi-do 12113 (KR)**

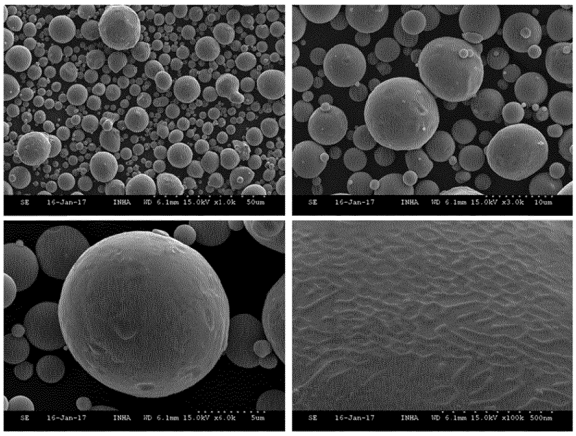
(72) Inventors:
- **LEE, Kwang Choon**
  **Seoul 04971 (KR)**
- **JANG, Bok Hyeon**
  **Gimpo-si**
  **Gyeonggi-do 10119 (KR)**

(74) Representative: **Nobbe, Matthias**
**Demski & Nobbe**
**Patentanwälte**
**Mülheimer Strasse 210**
**47057 Duisburg (DE)**

# (54) IRON-COPPER ALLOY HAVING HIGH THERMAL CONDUCTIVITY AND METHOD FOR MANUFACTURING SAME

(57) The present invention provides a high thermal conductivity iron-copper (Fe-Cu) alloy and a method of manufacturing the same. The present invention provides an iron-copper alloy containing 55 to 95 atomic% of iron and 5 to 45 atomic% of copper. The present invention also provides an iron-copper alloy manufacturing method including a first step of preparing a melting furnace; a second step of adding iron and copper to the melting furnace and performing dissolution and molten metal formation so as to contain 55 to 95 atomic% of iron and 5 to 45 atomic% of copper based on the weight of the iron-copper alloy; a third step of stabilizing the molten metal; and a fourth step of pouring the stabilized molten metal into a casting mold and performing casting. The present invention provides an iron-copper alloy that is an iron-based alloy containing iron as a main component and having high thermal conductivity and mechanical properties along with, for example, an electromagnetic-wave shielding property and a soft magnetic property, which can be widely used for metal parts and electronic parts and machine parts.

FIG. 2



EP 3 524 703 A1

## Description

[Technical Field]

**[0001]** The present invention relates to a new iron-copper (Fe-Cu) alloy containing iron (Fe) as a main component and an appropriate amount of copper (Cu), which has high thermal conductivity and mechanical properties along with, for example, an electromagnetic-wave shielding property and a soft magnetic property.

[Background Art]

**[0002]** Metal-related industries are replacing existing steel materials with lightweight material, such as aluminum (Al) alloys. The aluminum alloys are being widely employed for a variety of uses in many industrial fields owing to their excellent properties, including, for example, lightness in weight, thermal conductivity, corrosion resistance and ductility. The aluminum alloy having high thermal conductivity enables rapid cooling, thereby minimizing distortion or warpage of a molded article. Hence, the aluminum alloy can be useful as a molding material for injection molding or die casting.

**[0003]** For example, techniques of aluminum alloys for die casing have been proposed in Korean Patent Publication No.10-2015-0046014 and Korean Patent Registration No.10-1606525. The aluminum alloy contains aluminum (Al) as a main component and small amounts of silicon (Si), iron (Fe), manganese (Mn) and magnesium (Mg), and aluminum-silicon-magnesium (Al-Si-Mg) type alloys are widely used as molding materials for die casting.

**[0004]** However, the aluminum alloy has poor mechanical properties in view of strength or abrasion resistance. Accordingly, beryllium-copper (Be-Cu) alloys having high thermal conductivity and corrosion resistance and good mechanical properties, such as strength and abrasion resistance, are growing popular as molding materials. Techniques concerning the Be-Cu alloys are disclosed in Japanese Patent Publication No. JP 2003-003246, Korean Patent Publication Nos. 10-2012-0048287 and 10-2015-0053814, and so on.

**[0005]** The Be-Cu alloy is a practical alloy having high strength and high thermal conductivity and is advantageously used as molding materials for die casting. The Be-Cu alloy is generally obtained by repeatedly performing melt-casting beryllium (Be) and copper (Cu), performing a hot or cold plasticizing work, and performing annealing treatment, and cobalt (Co) is added to improve mechanical properties of the Be-Cu alloy. However, it is quite difficult to continuously cast the Be-Cu alloy and material costs of beryllium (Be) and copper (Cu) are very high, making a Be-Cu alloy manufacturing process uneconomic. Hence, the Be-Cu alloy is restrictively used in the manufacture of only premium products due to its high cost, thereby preventing its widespread application for general uses.

[Technical Problems to be Solved]

**[0006]** The present invention provides an iron-copper (Fe-Cu) alloy having improved properties with a new iron-based alloy composition, by which existing beryllium-copper (Be-Cu) alloys can be replaced, a method of manufacturing the same, and uses thereof.

**[0007]** Specifically, the present invention provides an iron-copper (Fe-Cu) alloy containing an appropriate amount of copper (Cu) in an iron (Fe) base, which has high thermal conductivity and mechanical properties along with, for example, an electromagnetic-wave shielding property and a soft magnetic property, a method of manufacturing the same, and uses thereof. In addition, the present invention provides materials containing the iron-copper alloy as uses of the iron-copper alloy.

[Technical Solutions]

**[0008]** To achieve the above and other objects, the present invention provides an iron-copper (Fe-Cu) alloy including 55 to 95 atomic % of iron, and 5 to 45 atomic % of copper.

**[0009]** In addition, the present invention provides an iron-copper (Fe-Cu) alloy including 80.5 to 95 atomic % of iron, and 5 to 19.5 atomic % of copper, wherein the iron-copper alloy has the following properties (a) to (c):

(a) thermal conductivity of greater than or equal to 70 W/m · K;
(b) tensile strength of greater than or equal to 300 N/mm$^2$; and
(c) hardness of greater than or equal to 100 HB.

**[0010]** In an exemplary embodiment, the iron-copper (Fe-Cu) alloy according to the present invention may have a spherical particle shape and may have a particle size of 0.1 μm to 150 μm.

**[0011]** In addition, the present invention provides a method of manufacturing an iron-copper (Fe-Cu) alloy, the method including a first step of preparing a melting furnace, a second step of adding iron and copper to the melting furnace and performing dissolution and molten metal formation so as to contain 55 to 95 atomic % of iron and 5 to 45 atomic % of copper based on the weight of the iron-copper alloy, a third step of stabilizing the molten metal, and a fourth step of pouring the stabilized molten metal into a casting mold and performing casting.

**[0012]** In an exemplary embodiment, the method may further include a fifth step of obtaining iron-copper alloy particles by remelting a casting obtained in the fourth step and then injecting the remelted casting.

**[0013]** In a preferred embodiment, the first step includes performing surface treatment for forming a porous impurity absorption layer on an inner surface of the melting furnace. Here, the impurity absorbent preferably contains zirconium silicate.

[Advantageous Effects]

**[0014]** As described above, according to the present invention, a new iron-based alloy which can replace existing beryllium-copper (Be-Cu) alloys is provided. The present invention can provide the iron-copper alloy that is an amorphous, complete molten alloy containing iron (Fe) as a main component and an appropriate amount of copper (Cu), which has high manufacturability and economic efficiency while having high thermal conductivity and excellent properties. In addition, the present invention can provide the iron-copper alloy having high thermal conductivity and mechanical properties along with, for example, an electromagnetic-wave shielding property and a soft magnetic property, which can be widely used for not only molding materials but also electronic parts and machine parts.

[Brief Description of Drawings]

**[0015]**

FIG. 1 shows a B-H curve (magnetization curve) of an iron-copper alloy prepared in Example of the present invention.
FIG. 2 shows scanning electron micrograph (SEM) photographs of iron-copper alloy particles prepared in Example 4 of the present invention according to magnification scales.
FIG. 3 shows an EDS analysis result of iron-copper alloy particles prepared in Example 4 of the present invention.
FIG. 4 shows an EDS analysis result of iron-copper alloy particles prepared in Example 5 of the present invention.
FIG. 5 shows an EDS analysis result of iron-copper alloy particles prepared in Example 6 of the present invention.
FIG. 6 shows an SEM photograph of a particle sample prepared in Comparative Example.

[Best Mode for Carrying Out the Invention]

**[0016]** As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items. In addition, as used herein, the term "at least one" is intended to include plural forms, i.e. one and more than two", unless the context clearly indicates otherwise.

**[0017]** In an embodiment, the present invention provides an iron-copper (Fe-Cu) alloy that is an iron based alloy containing iron (Fe) as a main component, which has a new alloy composition. According to another embodiment of the present invention, there is provided a method of manufacturing the iron-copper alloy.

**[0018]** In addition, according to a further embodiment of the present invention, there is provided a use of the iron-copper alloy that is a material containing at least the iron-copper alloy. For example, the material can be selected from a molding material and a material for a 3D printer.

**[0019]** The iron-copper alloy according to the present invention containing iron (Fe) and copper (Cu) is an iron based alloy having the iron (Fe) content higher than the copper (Cu) content, the iron-copper alloy comprising 55 to 95 atomic percentage (%) of iron (Fe) and 5 to 45 atomic percentage (%) of copper (Cu), based on the total weight of the iron-copper alloy. The content unit used in the present invention, i.e., "atomic percentage (at. %)", is based on the total weight of iron (Fe) and copper (Cu) atoms (sum of atomic weights of Fe and Cu), which can also be expressed in "volumetric percentage (vol. %)", as well known in the art. That is to say, in the present invention, at. % can also be expressed in vol. %.

**[0020]** In a preferred embodiment, metallic elements other than Fe and Cu are not contained in the iron-copper alloy according to the present invention. In addition, impurities, such as carbon (C) or oxygen (O), may be inevitably contained in the iron-copper alloy according to the present invention, but these impurities are contained in trace amounts. The impurities may be inevitably contained in an amount of, for example, not greater than 0.1 at. % (or vol. %), or not greater than 0.01 at. % (or vol. %).

**[0021]** The iron-copper alloy according to the present invention is an iron based alloy having copper contained in an appropriate amount and has improved properties owing to well coordination of the respective merits and advantages of iron and copper. The improved properties of the iron-copper alloy according to the present invention include at least high thermal conductivity and mechanical properties. Specifically, the iron-copper alloy according to the present invention has higher thermal conductivity and elasticity than existing iron alloys. In addition, the iron-copper alloy according to the present invention has higher hardness and abrasion resistance than existing copper alloys. In addition, since low-priced iron is used as a base (main component), the economic efficiency is high. Moreover, the iron-copper alloy according to the present invention has an electromagnetic-wave shielding property and soft magnetic property by appropriately adjusting the composition (content) of iron and copper, so that it can be used in a wide variety of applications. For example, the iron-copper alloy according to the present invention can be used for precision parts, such as solenoids, electromagnetic-wave shielding materials, and materials for 3D printers.

**[0022]** Hereinafter, a method of manufacturing the iron-copper alloy according to the present invention will be described with reference to embodiments of the iron-copper alloy according to the present invention. The manufacturing method that will be described below can easily implement the manufacture of the iron-copper alloy according to the present invention. However, the iron-copper alloy according to the present invention is not to be construed as being limited to the following manufacturing methods.

**[0023]** The method of manufacturing the iron-copper alloy (to be abbreviated as, "manufacturing method," hereinafter) according to the present invention includes a first step of preparing a melting furnace, a second step of adding iron and copper to the melting furnace and performing dissolution and molten metal formation, a third step of stabilizing the molten metal, and a fourth step of pouring the stabilized molten metal into a casting mold and performing casting. Optionally, the manufacturing method according to the present invention may further include a fifth step of obtaining an iron-copper alloy existing in powdered particles from the casting obtained in the fourth step. An embodiment of the manufacturing method according to the present invention will now be described with respect to various processing steps.

(1) Preparation of melting furnace (First step)

**[0024]** As described above, the iron-copper alloy according to the present invention contains 55 to 95 at. % of iron (Fe) and 5 to 45 at. % of copper (Cu). The alloy composition specified in the present invention is not a theoretical molten alloy composition. That is to say, the alloy composition specified in the present invention is a proportion in which the Fe content exceeds a theoretical amount of iron (Fe) alloyed. Such an alloy composition can be implemented in a case of manufacturing a master alloy using sintering. However, it is difficult to achieve amorphous, complete alloy formation by melting through dissolution (molten metal formation). In general, iron and copper can be melted and alloyed when the Fe content is smaller than the Cu content (for example, the Fe content being less than 2.5 vol. %). In the alloy composition specified in the present invention, however, separation of two phases, i.e., a Fe-rich phase and a Cu-rich phase, may occur to the molten metal, resulting in segregation (one of the two metals being biased to one place), which makes it difficult to achieve uniformly-distributed, complete molten alloy formation.

**[0025]** The present inventor repeatedly conducted intensive and thorough research on methods for forming a complete molten alloy having a high Fe content, resulted in the finding that the complete molten alloy without segregation (being biased) can be formed when impurity content is minimized with the Cu content titrated, and/or when a dissolution process is modified. In the present invention, complete molten alloy formation can be achieved by improving a melting furnace and/or by improving a raw material adding method during dissolution according to a specific embodiment.

**[0026]** In the first step, one embodiment for solving the objective of the present invention is provided. In the first step, the melting furnace for forming the iron-copper molten metal is prepared. Here, a high-frequency inductively heated melting furnace, which enables fast dissolution by being rapidly heated, may be used as the melting furnace. In addition, the melting furnace is preferably a ceramic melting furnace including magnesium as a main component. For example, a melting furnace manufactured by performing high-temperature firing on a ceramic material containing, for example, magnesium oxide as a main component, may be used as the ceramic melting furnace.

**[0027]** In a preferred embodiment, the melting furnace is used in such a manner that a porous impurity absorption layer is formed on its inner surface. In detail, the first step includes preparing a high-frequency inductively heated ceramic melting furnace and performing surface treatment for forming a porous impurity absorption layer on the inner surface of the ceramic melting furnace. Here, the impurity absorption layer is entirely or partially formed on the inner surface of the melting furnace, specifically on at least internal bottom surface and/or an internal wall surface of the melting furnace, which is a surface being in contact with the molten metal.

**[0028]** In addition, the impurity absorption layer includes at least an impurity absorbent. In detail, in the step of performing surface treatment, an absorption layer composition including the impurity absorbent, a resin and a solvent, is coated on the inner surface of the melting furnace, followed by firing, thereby forming the porous impurity absorption layer. According to the present invention, impurities contained in the iron-copper molten metal (e.g., C, O, etc.) can be absorbed by the porous impurity absorption layer for removal, thereby attaining a complete alloy without segregation (being biased) even with the non-theoretical alloy composition. The porous impurity absorption layer may have a thickness, for example, in the range from 0.5mm to 2 mm, but aspects of the present invention are not limited thereto.

**[0029]** The impurity absorbent is not particularly limited as long as it can absorb and remove impurities contained in the iron-copper molten metal (e.g., C, O, etc.). The impurity absorbent is in the form of powders having a particle size in the range from, for example, 50 $\mu$m to 500 $\mu$m. The impurity absorbent may be selected from a metal oxide and/or a metal. The impurity absorbent preferably includes at least one selected from zirconium silicate and aluminum (Al). More preferably, zirconium silicate and aluminum (Al) can be both used as the impurity absorbent. Here, the aluminum (Al) may have high purity of at least 99.8% by weight (to be abbreviated as wt. %). In the present invention, the zirconium silicate and aluminum (Al) are preferably used as impurity absorbents because they are more effective than other metal oxides or metals in completely removing the impurities contained in the molten metal. In detail, the zirconium silicate and aluminum (Al) can completely remove impurities contained in the molten metal, thereby forming high-purity molten metal alloy containing only iron and copper, which can be confirmed by the following examples.

**[0030]** In addition, the resin is not particularly limited as long as it has adhesiveness. The resin, which offers initial adhesion between the inner surface of the melting furnace and the impurity absorption layer while providing cohesion between powder particles of the impurity absorbent, is preferably used. In addition, the resin is removed by high-temperature heat derived from firing, thereby imparting porosity to the impurity absorption layer. The resin may be selected from a synthetic resin and/or a natural resin. The resin may exist in a solid phase and/or a liquid phase. Examples of the resin may include at least one polymer and/or copolymers thereof, which are selected from the group consisting of an acryl-based resin, a vinyl-based resin, an epoxy-based resin, an urethane-based resin, a silicone-based resin, an olefin-based resin, an ester-based resin, a rubber-based resin, and so on.

**[0031]** A butadiene-styrene-alkyl methacrylate copolymer is preferably used as the resin. Specific examples of the butadiene-styrene-alkyl methacrylate copolymer may be selected from the group consisting of a butadiene-styrene-methyl methacrylate copolymer, a butadiene-styrene-ethyl methacrylate copolymer and/or a butadiene-styrene-butyl methacrylate copolymer. In an exemplary embodiment, the butadiene-styrene-alkyl methacrylate copolymer useful in the present invention may have a particle size in the range from 50 nm to 500 nm. When a butadiene-styrene-alkyl methacrylate copolymer is selected as the resin and is nano-sized, it can be rapidly removed through firing and can be evenly distributed in the powdered impurity absorbent. Accordingly, the adhesion of the impurity absorbent can be improved, and a uniform microporous structure is formed in the impurity absorption layer, thereby improving impurity absorbing/removing capability.

**[0032]** The solvent, which is associated with dispersibility and coating performance, may be selected from hydrocarbon-based solvents. Examples of the solvent may be selected from alcohols and/or ketones.

**[0033]** In addition, in an exemplary embodiment, the absorption layer composition may include 50 wt. % to 80 wt. % of an impurity absorbent, 5 wt. % to 20 wt. % of a resin, and 15 wt. % to 40 wt. % of a solvent. Here, when the content of the impurity absorbent is less than 50 wt. %, the impurity absorbing/removing capability may be negligible, and when the content of the impurity absorbent is greater than 80 wt. %, the porosity and coating performance may be degraded. In addition, when the content of the resin is less than 5 wt. %, the porosity and coating performance may be degraded, and when the content of the resin is greater than 20 wt. %, the content of the impurity absorbent is relatively reduced, so that the impurity absorbing/removing capability may become negligible. In addition, in consideration of dispersibility and coating performance, the content of the solvent is preferably in the range stated above.

**[0034]** As described above, in a case where the porous impurity absorption layer is formed on the inner surface of the melting furnace in the first step, the impurities contained in the molten metal can be absorbed and removed during dissolution, thereby enabling homogenized, complete iron-copper alloy formation and effectively obtaining a high-purity iron-copper alloy containing little impurities.

(2) Performing dissolution (Second step)

**[0035]** Alloying materials, i.e., iron and copper, are added to the melting furnace. Here, high-purity iron and high-purity electrolytic copper may be used as the alloying materials. The temperature of the melting furnace may be raised by high-frequency inductively heating by applying power to the melting furnace. The melting furnace is preferably maintained in a temperature range in which iron and copper can be dissolved. For example, the melting furnace is preferably maintained at a temperature in the range from approximately 1,520°C to approximately 1,650°C by being rapidly heated using the high-frequency inductively heating. During the dissolution, stirring may be performed.

**[0036]** In addition, in the second step, iron and copper are added to the melting furnace to then perform dissolution to form a molten metal so as to contain 55 to 95 at. % of iron and 5 to 45 at. % of copper, based on the total weight of the finally produced iron-copper alloy. In detail, when the amounts of iron and copper added to the melting furnace are 55 to 95 vol. % and 5 to 45 vol. % in total (i.e., Fe:Cu = 55 to 95:5 to 45 in a volume ratio), the alloy composition may be obtained. Here, when the content of copper is less than 5 at. % (or vol. %), improving effects of various properties including, for example, thermal conductivity, corrosion resistance and/or electromagnetic-wave shielding property, may be insignificant. In addition, when the content of copper is greater than 45 at. % (or vol. %), the content of iron is relatively reduced, so that mechanical properties including, for example, hardness and/or abrasion resistance may be degraded.

**[0037]** In light of the foregoing, in a preferred embodiment of the present invention, in consideration of the foregoing, iron and copper are preferably added to the melting furnace to then perform dissolution to form a molten metal in the second step so as to contain 80.5 to 95 at. % of iron and 5 to 19.5 at. % of copper, based on the total weight of the final product, that is, the iron-copper alloy. That is to say, when the amounts of iron and copper added to the melting furnace are 80.5 to 95 vol. % and 5 to 19.5 vol. % in total (i.e., Fe:Cu = 80.5 to 95:5 to 19.5 in a volume ratio), the alloy composition may be obtained. In this case, the alloy composition may have excellent thermal conductivity, mechanical properties, electromagnetic-wave shielding property and/or soft magnetic property.

**[0038]** In an embodiment, when iron and copper are added to the melting furnace, iron and copper may be initially added in a volume ratio of 1:1 to then be rapidly dissolved while stirring, followed by additionally adding iron to the melting furnace to have the alloy composition. That is to say, it is desirable to obtain a uniformly-distributed iron-copper alloy by adding iron and copper in the volume ratio of 1:1 at an initial stage and additionally adding iron at a later stage, rather than by adding iron and copper at a time. In addition, when iron is additionally added, it is desirable to intermittently add iron little by little. That is to say, in order to obtain a uniformly-distributed iron-copper molten alloy, it is advantageous to additionally add small amounts of iron over several times.

**[0039]** In addition, the second step (dissolution) may be performed while deoxidizing (preventing oxidation) by adding a deoxidizer to the melting furnace in a conventional manner. In addition, a flux may further be added in the second step (dissolution), like in a conventional method. Here, as the deoxidizer and the flux, any deoxidizer and any flux generally used in the related art may be used. For example, at least 99.8 wt. % of high-purity Al and/or high-purity Ti, may be used as the deoxidizer, and $Al_2O_3$, CaO and/or $SiO_2$ may be used as the flux.

(3) Stabilizing (Third step)

**[0040]** The molten metal resulting from the dissolution is stabilized. The stabilization may be performed such that the molten metal is left undisturbed in the melting furnace for a predetermined time while shutting off the power supply. For example, the stabilization may be performed by maintaining the molten metal at a temperature in the range from 1,450°C to 1,520°C and leaving the molten metal undisturbed. As the result of the stabilization, homogenization of iron and copper may be achieved.

(4) Casting (Fourth step)

**[0041]** The stabilized molten metal is poured into a casting mold to cast the same into an alloy casting having a predetermined shape. The fourth step (casting) is performed in accordance with a general process. The casting mold is not particularly limited in shape, and may be shaped of an ingot or a cast piece. In some cases, the casting mold may be shaped of a ready-to-use product. In addition, the casting mold may have a cooling function, like a conventional casting mold.

**[0042]** In addition, the casting obtained in the fourth step may be subjected to post treatment through a general post treatment process, such as heat treatment and/or cooling. Specifically, the casting may be post-treated by, for example, annealing, normalizing, quenching and/or tempering. The post treatment may be appropriately selected according to the use and product to be applied. For example, in a case of a product requiring a mechanical strength (tensile strength, hardness, etc.), quenching and tempering may be performed. In addition, the casting may have a variety of shapes through remelting and/or post-processing, and may be processed into a ready-to-use product or a half-finished product.

(5) Granulating (Fifth step)

**[0043]** The fifth step is an optional process, which is performed to obtain powdered iron-copper alloy particles. In the fifth step, the casting obtained in the fourth step (casting) is remelted and injected, thereby obtaining the powdered iron-copper alloy particles. In detail, the fifth step may include remelting the casting, injecting the remelted casting and granulating the same to obtain the powdered iron-copper alloy particles.

**[0044]** Here, the same melting furnace as used in the first step may be used in the remelting step. In addition, in order to prevent the iron-copper alloy from being oxidized in the remelting of the fifth step, the remelting is preferably performed in a vacuum melting furnace. That is to say, a vacuum furnace may be used as the melting furnace. The casting may be remelted in the vacuum furnace at a temperature in the range from 1,600°C to 1,700°C. In the granulating step, the remelted casting can be made into powdered particles by injecting the remelted casting at a temperature in the range from 1,400°C to 1,500°C. Here, the powdered particles may have a particle size, for example, in the range from 0.1 $\mu$m to 150 $\mu$m. The obtained powdered iron-copper alloy particles are preferably spherical particles.

**[0045]** According to the above-described manufacturing method, complete alloy formation can be achieved without segregation (being biased) even with a non-theoretical alloy composition containing 55 to 95 at. % of iron (Fe) and 5 to 45 at. % of copper (Cu). In addition, the respective merits and advantages of iron and copper are well coordinated in the iron-copper alloy manufactured according to the present invention, so that the iron-copper alloy may have high thermal conductivity and mechanical properties, such as tensile strength, hardness, abrasion resistance, or the like, along with, for example, an electromagnetic-wave shielding property and a soft magnetic property, as described above.

Therefore, the iron-copper alloy can be widely used for a variety of purposes.

**[0046]** In a preferred embodiment, the iron-copper alloy according to the present invention may contain 80.5 to 95 at. % (or vol. %) of iron and 5 to 19.5 at. % (or vol. %) of copper. More specifically, the iron-copper alloy according to the present invention may contain 82.5 to 90.5 at. % (or vol. %) of iron and 9.5 to 17.5 at. % (or vol. %) of copper. In this case, properties of the iron-copper alloy, including thermal conductivity, mechanical properties, electromagnetic-wave shielding property and/or soft magnetic property, may be effectively improved.

**[0047]** In addition, the iron-copper alloy according to the present invention may have the following properties (a) to (c). When the iron-copper alloy according to the present invention has the following properties (a) to (c), the iron-copper alloy can be generally used not only as a molding material for injection molding or die casting but also as a material for a 3D printer:

(a) thermal conductivity of 70 W/m · K or higher;
(b) tensile strength of 300 N/mm$^2$ or greater; and
(c) hardness of 100 HB or greater.

**[0048]** The thermal conductivity, tensile strength and hardness may be determined in accordance with a general measuring method. The thermal conductivity may be a value measured at room temperature (20°C to 25°C) in conformity with the ASTM E1461 standard (Laser flash: Thru-Plane thermal conductivity). In addition, the tensile strength may be measured in conformity with the KS B 0801 standard and the hardness may be measured in conformity with the KS B 0805 standard.

**[0049]** Specifically, the iron-copper alloy may have a thermal conductivity in the range from 70 to 150 W/m · K, for example. In addition, the iron-copper alloy may have a tensile strength, for example, in the range from 300 to 1,350 N/mm$^2$. In addition, the iron-copper alloy may have a hardness, which is a Brinell hardness, in the range from 100 HB to 400 HB. The respective properties of the iron-copper alloy may be optimized according to the use in applied fields. For example, the tensile strength and hardness can be increased by the aforementioned post treatment (e.g., normalizing, quenching, tempering, and so on). After the post treatment, the iron-copper alloy may have a tensile strength of 500 N/mm$^2$ or greater and a hardness of 200 HB or greater.

**[0050]** In an exemplary embodiment, along with the properties (a) to (c), the iron-copper alloy according to the present invention may have (d) magnetic permeability of 45 to 650 $m_m$. The magnetic permeability may be determined in accordance with a general measuring method for a magnetic material (e.g., metals, etc.), and may be a value measured at a low frequency of 50 Hz. In addition, the iron-copper alloy according to the present invention preferably is in a spherical particle shape. The spherical particle shape can be implemented through the fifth step. Here, the iron-copper alloy according to the present invention has a spherical particle shape and may have a particle size in the range, for example, from 0.1 μm to 150 μm. As described above, when the iron-copper alloy is in the spherical particle shape, it can be useful as a material for 3D printer. In the present invention, the term "spherical" used is not to be construed as being perfectly spherical but is to be construed as being "quasi-spherical" as well as "perfectly spherical".

**[0051]** In the present invention, "spherical particles" suggest that iron and copper are uniformly distributed in the alloy without segregation (being biased) and complete molten alloy formation is achieved even if the iron-copper alloy has a non-theoretical alloy composition. In this respect, the spherical particles are technically significant. That is to say, when complete molten alloy formation is not achieved, spherical particles can be hardly obtained through injecting process. In the present invention, the spherical particles may also have technical significance in that an iron-copper alloy molded article having a uniform composition through remelting can be manufactured.

**[0052]** Meanwhile, the iron-copper alloy according to the present invention can be widely employed for a variety of application fields and uses, and the application fields and uses are not particularly limited. As described above, the iron-copper alloy according to the present invention may be used not only as a molding material but also as electronic parts, high-temperature machine parts, precision machine parts, materials for 3D printers, and so on. In addition, the iron-copper alloy according to the present invention can be widely employed in various fields, including electric materials, electromagnetic-wave shielding materials, anti-microbial materials, sensor materials, medical tools for surgery, energy related fields, coating fields, and so on.

**[0053]** Hereinafter, Examples of the present invention and Comparative Examples will be described. The following Examples are provided only by way of example for a better understanding of the present invention, but the present invention is not limited by those examples. In addition, the following Comparative Examples do not represent prior art but are provided only for comparison with Examples of the present invention.

## Example 1

<Melting Furnace>

**[0054]** A ceramic melting furnace containing magnesium as a main component was prepared as a high-frequency inductively heated melting furnace. Thereafter, a porous impurity absorption layer was formed on an inner wall surface and a bottom surface of the prepared melting furnace. The porous impurity absorption layer was formed by coating an absorption layer composition to a thickness of approximately 1 mm, the composition prepared by mixing 65 wt. % of an impurity absorbent, 15 wt. % of a resin, and 30 wt. % of a solvent, based on the total weight of the composition, and then heating at a temperature of approximately 1,150°C for firing. Here, zirconium silicate ($ZrSiO_4$) and Al powder were used as the impurity absorbent, a butadiene-styrene-alkyl methacrylate copolymer was used as the resin, and isopropyl alcohol was used as the solvent.

<Molten metal/Stabilization/Casting>

**[0055]** Iron (pure iron having purity of approximately 99.9 wt. %) and electrolytic copper having purity of approximately 99.9 wt. %) were added to the melting furnace in a volume ratio of 1:1 at an initial stage, and rapid dissolution was performed by increasing output power while stirring. Here, the dissolution was performed while deoxidizing (preventing oxidation) by intermittently adding a deoxidizer (Al) to the melting furnace. In addition, it was confirmed through observation with naked eye whether Fe and Cu added to the melting furnace were completely dissolved, Fe was additionally added to the melting furnace little by little to increase the Fe content, and Fe and Cu were completely dissolved at a temperature of approximately 1,550°C. Thereafter, stabilization was performed such that the molten metal was left undisturbed in the melting furnace until the temperature of the melting furnace was raised up to approximately 1,500°C while shutting off the power supply. Next, the stabilized molten metal was poured into a casting mold, followed by cooling, thereby obtaining an iron-copper alloy ingot.

## Examples 2 and 3

**[0056]** Iron-copper alloy ingots were prepared in substantially the same manner as in Example 1, except that amounts of iron additionally added during dissolution were changed for the purpose of making final alloy compositions (atomic percentages of iron and copper) differ from the alloy composition of Example 1.

## Comparative Example 1

**[0057]** An iron-copper alloy ingot was prepared in substantially the same manner as in Example 1, except that a different kind of impurity absorbent was used in forming a porous impurity absorption layer on the inner surface of the melting furnace. In detail, zirconium silicate ($ZrSiO_4$) and zirconium oxide ($ZrO_2$), instead of aluminum (Al), were used as the impurity absorbent.

## Comparative Example 2

**[0058]** Unlike in Example 1, iron and copper were added to a melting furnace in a volume ratio of 9:1 at a time, and an iron-copper alloy used in Comparative Example 2 was prepared by performing dissolution without forming a porous impurity absorption layer on an inner surface of the melting furnace.

**[0059]** Elemental analyses were carried out on the obtained iron-copper alloy samples in the following manner, and the results are shown in Table 1. In addition, thermal conductivity, tensile strength, hardness and magnetic permeability of each alloy sample were evaluated, and the results are also shown in Table 1. The thermal conductivity was measured by measuring a density, specific heat and thermal diffusivity of each alloy sample, which is a thermal conductivity measuring method of a metal sample, and then evaluated in conformity with the ASTM E1461 standard (Laser flash: Thru-plane thermal conductivity). Here, all tests were carried out at a temperature of 25°C. In addition, the tensile strength was evaluated in conformity with the KS B 0801 standard, and the hardness (Brinell hardness) was evaluated in conformity with the KS B 0805 standard. The magnetic permeability was evaluated at a frequency of 50 Hz using a magnetic permeability tester (BHU-60 model manufactured by Riken Denshi Co., Ltd., Japan).

<Elemental analysis>

**[0060]** Weighed alloy samples were placed in a glass beaker and 10 mL of an aqua regia (an aqueous solution of hydrochloric acid and sulfuric acid) was added thereto for dissolution. Then, elemental analysis was conducted such that iron and copper were quantified and their concentrations contained in the respective samples were determined through inductively coupled plasma-atomic emission spectroscopy (ICP-AES) under the following measurement conditions.

* Measurement conditions of ICP-AES

- Measuring device: PerkinElmer Optima 5300 DV
- Measurement wavelength: 238.204 nm (Fe), 327.393 nm (Cu)
- Quantitative method: Internal standard method

Table 1: Elemental analysis and property evaluation of Fe-Cu alloys

|  | Impurity absorbent | Composition (at. %) |  | Thermal conductivity [W/m · K] | Tensile strength [N/mm$^2$] | Brinell hardness [HB] | Magnetic permeability [$m_m$] |
|---|---|---|---|---|---|---|---|
|  |  | Fe | Cu | Thermal conductivity [W/m · K] | Tensile strength [N/mm$^2$] | Brinell hardness [HB] | Magnetic permeability [$m_m$] |
| Exam. 1 | $ZrSiO_4$ + Al | 89.58 | 10.42 | 74.3 | 327 | 154 | 630 |
| Exam. 2 | $ZrSiO_4$ + Al | 88.32 | 11.68 | 76.6 | 323 | 143 | 613 |
| Exam. 3 | $ZrSiO_4$ + Al | 90.07 | 9.93 | 70.5 | 342 | 161 | 637 |
| Comp. Exam. 1 | $ZrO_2$ | Segregation |  | 56.1 | Cracks | - | - |
| Comp. Exam. 2 | - | Segregation |  | 47.3 | Cracks | - | - |

**[0061]** As shown in Table 1, it was confirmed that the iron-copper alloys prepared in Examples had higher thermal conductivity (70 W/m · K or higher) than those prepared in Comparative Examples. In addition, each of the iron-copper alloys prepared in Examples had a tensile strength of 300 N/mm$^2$ or greater and hardness of 140 HB or greater. Here, the high tensile strength of 320 N/mm$^2$ or greater means that a uniformly-distributed, complete iron-copper alloy was formed without segregation (being biased). In addition, the iron-copper alloys prepared in Examples demonstrated magnetic permeability of approximately 600 $m_m$, suggesting that they had electromagnetic-wave shielding capability. FIG. 1 shows a B-H curve (magnetization curve) of an iron-copper alloy prepared in Example of the present invention, suggesting that the iron-copper alloy prepared in Example 1 had a soft magnetic property.

**[0062]** However, in Comparative Examples, complete alloy formation was not achieved and segregation occurred to the alloys. In addition, cracks were generated due to segregation, making it impossible to measure the tensile strength of each of the alloys prepared in Comparative Examples. In addition, since elements of the respective alloys prepared in Comparative Examples were not uniformly distributed due to segregation, accurate elemental analyses were not made and the results thereof are not given in Table 1. For the same reason, the hardness and magnetic permeability of the alloy samples in Comparative Examples are not given in Table 1, either.

**[0063]** Table 2 shows property evaluation results according to post treatment, the evaluation results shown before and after treatment performed specifically on the same alloy sample with the sample prepared in Example 2. The post treatment was conducted in a general manner by performing annealing, normalizing, quenching and tempering.

Table 2: Property changes depending on post treatment of iron-copper alloys

| | Before treatment (Exam. 2) | After treatment | | | |
|---|---|---|---|---|---|
| | | Annealing | Normalizing | Quenching (900°C) + tempering | Quenching (1,050°C) + tempering |
| Tensile strength [N/mm$^2$] | 323 | 301 | 604 | 1,016 | 1,311 |
| Elongation [%] | 10 | 30 | 15 | 3 | 1 |
| Brinell hardness [HB] | 143 | 100 | 207 | 282 | 374 |

**[0064]** As shown in Table 2, it was confirmed that the iron-copper alloy experienced property changes after post treatment. For example, when the post treatment of quenching (and tempering) was performed at a temperature of 1,050°C, the iron-copper alloy had a tensile strength of 1,300 N/mm$^2$ or greater and a hardness of 370 HB or greater, suggesting that the mechanical strength of the iron-copper alloy was improved, compared to a case where the post treatment was not performed. As described above, the iron-copper alloy demonstrated improved mechanical strengths through heat treatment, like a general pure single metal (e.g., pure iron, etc.), suggesting that complete alloy formation was achieved by performing the post treatment on the iron-copper alloy.

**Examples 4-6**

**[0065]** Iron-copper alloy ingots were prepared in substantially the same manner as in Example 1, except that amounts of iron additionally added during dissolution were changed for the purpose of making final alloy compositions (atomic percentages of iron and copper) differ from the alloy composition of Example 1. In addition, in Examples 4-6, the iron-copper alloy ingots obtained through casting were granulated in the following manner to prepare powdered iron-copper alloy particles.

**[0066]** First, iron-copper alloy ingots according to Examples 4-6, which were obtained through casting, were placed in a high-frequency inductively heated melting furnace, and maximum power was applied thereto to perform remelting at a temperature of approximately 1,650°C. Here, the melting furnace was maintained in a vacuum state to prevent oxidation. Next, the remelted casting was granulated by injecting the same into an injection chamber using an injector. Here, the injection chamber was maintained in an argon (Ar) gas atmosphere to prevent oxidation, and the remelted casting was injected at a temperature of 1,450°C, thereby manufacturing the powdered iron-copper alloy particles.

**[0067]** FIGS. 2 to 5 show scanning electron micrograph (SEM) photographs of powdered iron-copper alloy particles prepared in Examples 4 to 6 of the present invention. Specifically, FIG. 2 shows scanning electron micrograph (SEM) photographs of iron-copper alloy particles prepared in Example 4 of the present invention according to magnification scales, and FIG. 3 shows an EDS analysis result of iron-copper alloy particles prepared in Example 4 of the present invention. In addition, FIG. 4 shows an EDS analysis result of iron-copper alloy particles prepared in Example 5 of the present invention, and FIG. 5 shows an EDS analysis result of iron-copper alloy particles prepared in Example 6 of the present invention.

**[0068]** As shown in FIG. 2 to 5, the iron-copper alloy particles manufactured according to Examples 4-6 are fine particles of a particle size of 30 μm or less, which have an almost perfectly spherical shape. As shown from three photographs in the lower part of FIG. 3 showing distributions of iron and copper (iron: red; copper: green), iron and copper are uniformly distributed without segregation (being biased). Among the three photographs in the lower part of FIG. 3, the middle photograph shows a distribution of iron (red), the right photograph shows a distribution of copper (green), and the left photograph shows a distribution of iron and copper. In this way, the iron-copper alloy particles having perfectly spherical shapes and showing a uniform distribution suggest that iron and copper were completely alloyed.

**[0069]** FIG. 6 shows an SEM photograph of a particle sample using an ingot prepared in Comparative Example 2. As shown in FIG. 6, in Comparative Example 2, the particles had shapes of amorphous pieces due to segregation, suggest that iron and copper were not completely alloyed.

## Claims

1. A method of manufacturing an iron-copper (Fe-Cu) alloy, the method comprising:

a first step of preparing a melting furnace;
a second step of adding iron and copper to the melting furnace and performing dissolution and molten metal formation so as to contain 55 to 95 atomic % of iron and 5 to 45 atomic % of copper based on the weight of the iron-copper alloy;
a third step of stabilizing the molten metal; and
a fourth step of pouring the stabilized molten metal into a casting mold and performing casting.

**2.** The method of claim 1, further comprising a fifth step of obtaining iron-copper alloy particles by remelting a casting obtained in the fourth step and then injecting the remelted casting.

**3.** The method of claim 1, wherein the second step comprises performing dissolution of iron and copper while maintaining the melting furnace at a temperature in the range from 1,520°C to from 1,650°C, and the third step comprises stabilizing the iron-copper molten metal by maintaining the melting furnace at a temperature in the range from 1,450°C to 1,520°C.

**4.** The method of claim 2 wherein the fifth step comprises:

remelting the casting obtained in the fourth step in a vacuum melting furnace at a temperature in the range from 1,600°C to 1,700°C; and
granulating the remelted casting by injecting the remelted casting at a temperature in the range from 1,400°C to 1,500°C to obtain iron-copper alloy particles having a particle size of 0.1 $\mu$m to 150 $\mu$m.

**5.** The method of claim 1, wherein the first step comprises performing surface treatment for forming a porous impurity absorption layer on an inner surface of the melting furnace.

**6.** The method of claim 5, wherein the performing of the surface treatment comprises coating an absorption layer composition containing an impurity absorbent, a resin and a solvent on the inner surface of the melting furnace, followed by firing, to form the porous impurity absorption layer.

**7.** The method of claim 6, wherein the impurity absorbent contains one or more selected from zirconium silicate and aluminum (Al).

**8.** An iron-copper (Fe-Cu) alloy comprising:

55 to 95 atomic % of iron; and
5 to 45 atomic % of copper.

**9.** An iron-copper (Fe-Cu) alloy comprising:

55 to 95 atomic % of iron; and
5 to 45 atomic % of copper,
wherein iron and copper are dissolved in a melting furnace having a porous impurity absorption layer formed on its inner surface to form an iron-copper molten alloy.

**10.** The iron-copper (Fe-Cu) alloy of claim 9, wherein the porous impurity absorption layer contains one or more selected from zirconium silicate and aluminum (Al).

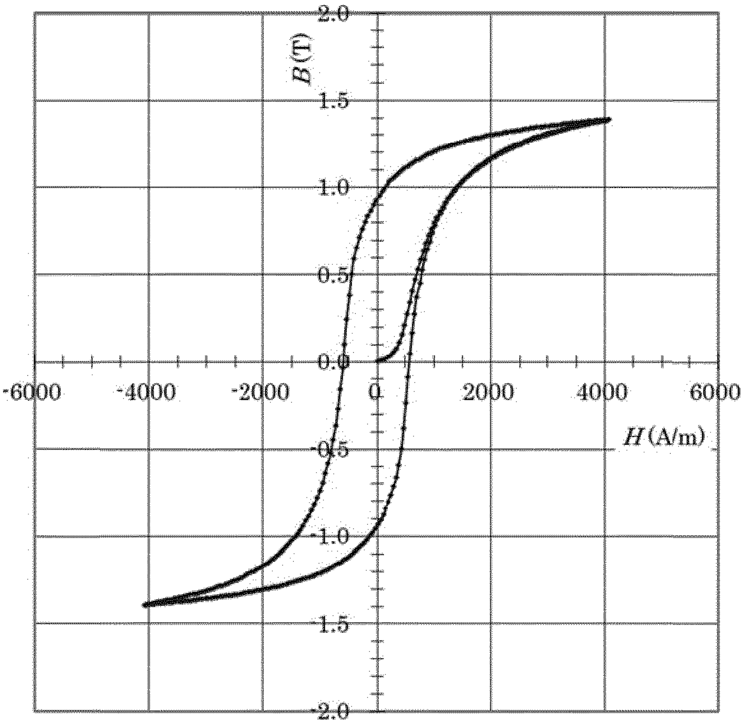
**11.** The iron-copper (Fe-Cu) alloy of claim 8, which comprises:

80.5 to 95 atomic % of iron; and
5 to 19.5 atomic % of copper,
wherein the iron-copper alloy has the following properties (a) to (c):

(a) thermal conductivity of greater than or equal to 70 W/m · K;
(b) tensile strength of greater than or equal to 300 N/mm$^2$; and
(c) hardness of greater than or equal to 100 HB.

**12.** The iron-copper (Fe-Cu) alloy of one of claims 8 to 11, which has a spherical particle shape and has a particle size of 0.1 μm to 150 μm.

FIG. 1



B-H curve

FIG. 2

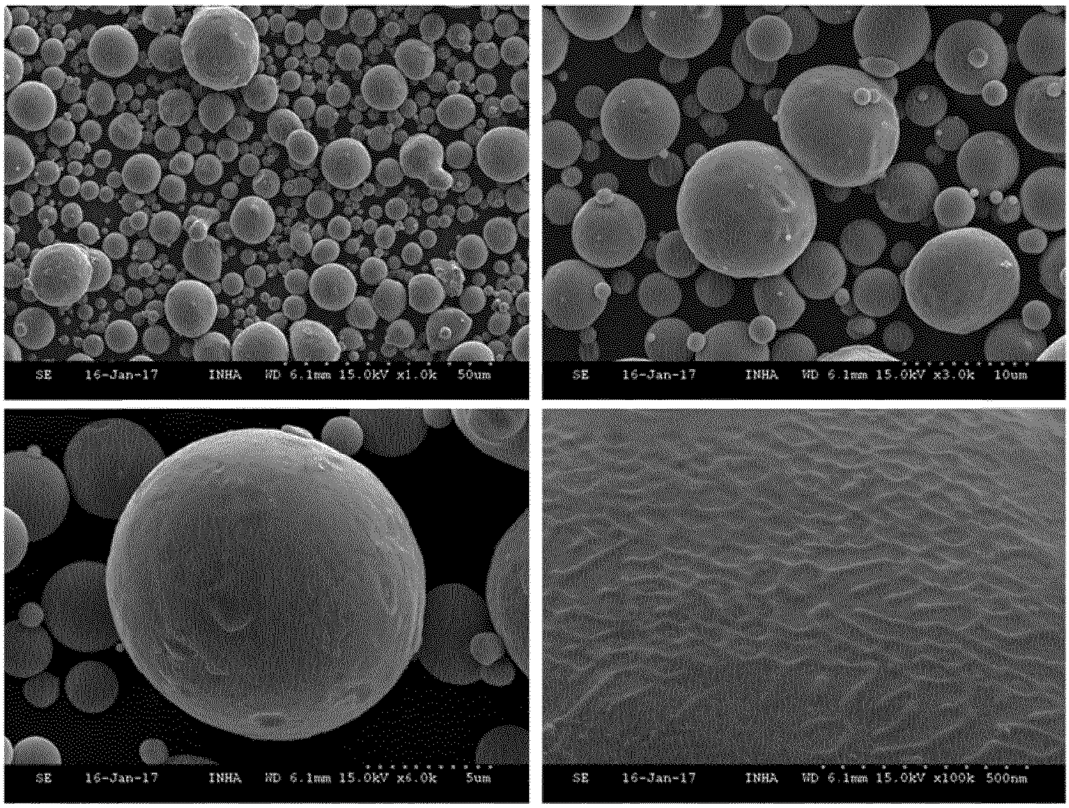
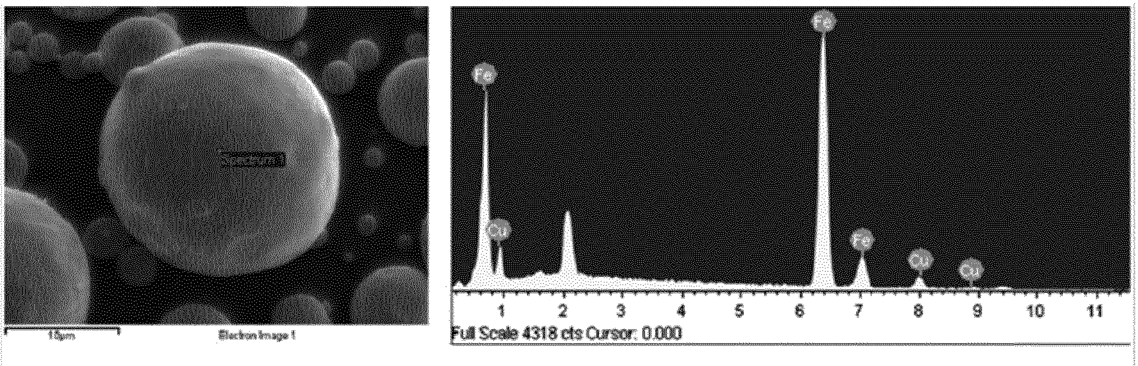


FIG. 3



| Element | App Conc. | Intensity Corrn. | Weight% | Weight% | Atomic% |
|---|---|---|---|---|---|
| Fe K | 66.48 | 0.9818 | 80.84 | 0.87 | 82.76 |
| Cu L | 2.79 | 0.1736 | 19.16 | 0.87 | 17.24 |
| Totals | | | 100.00 | | |

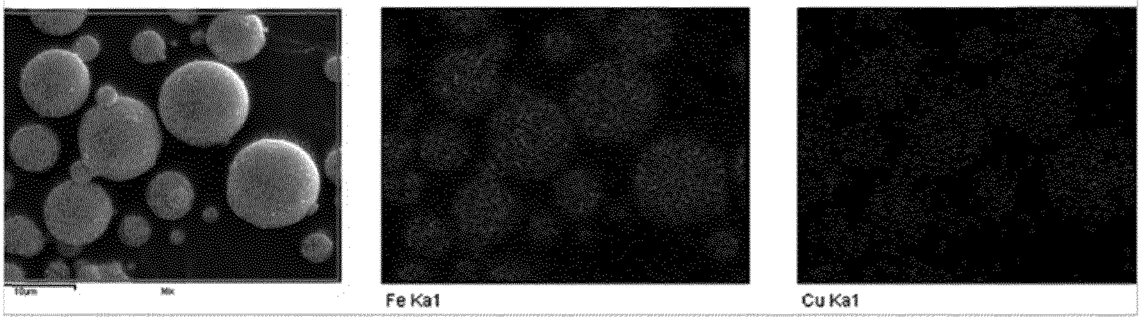


FIG. 6

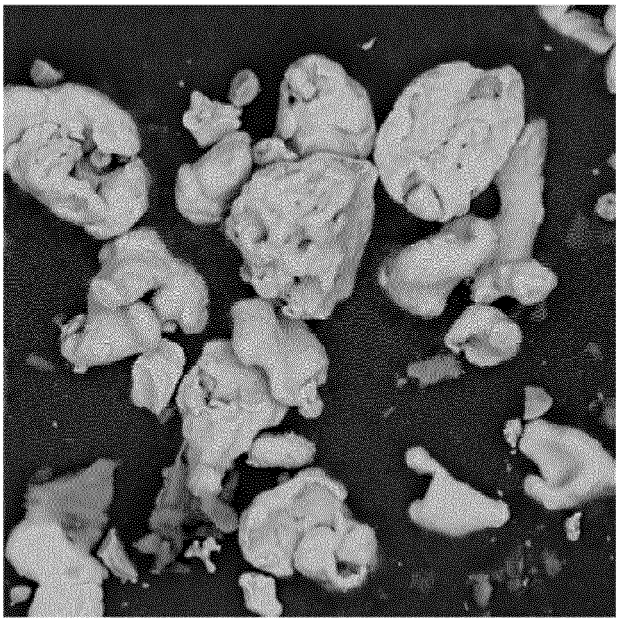
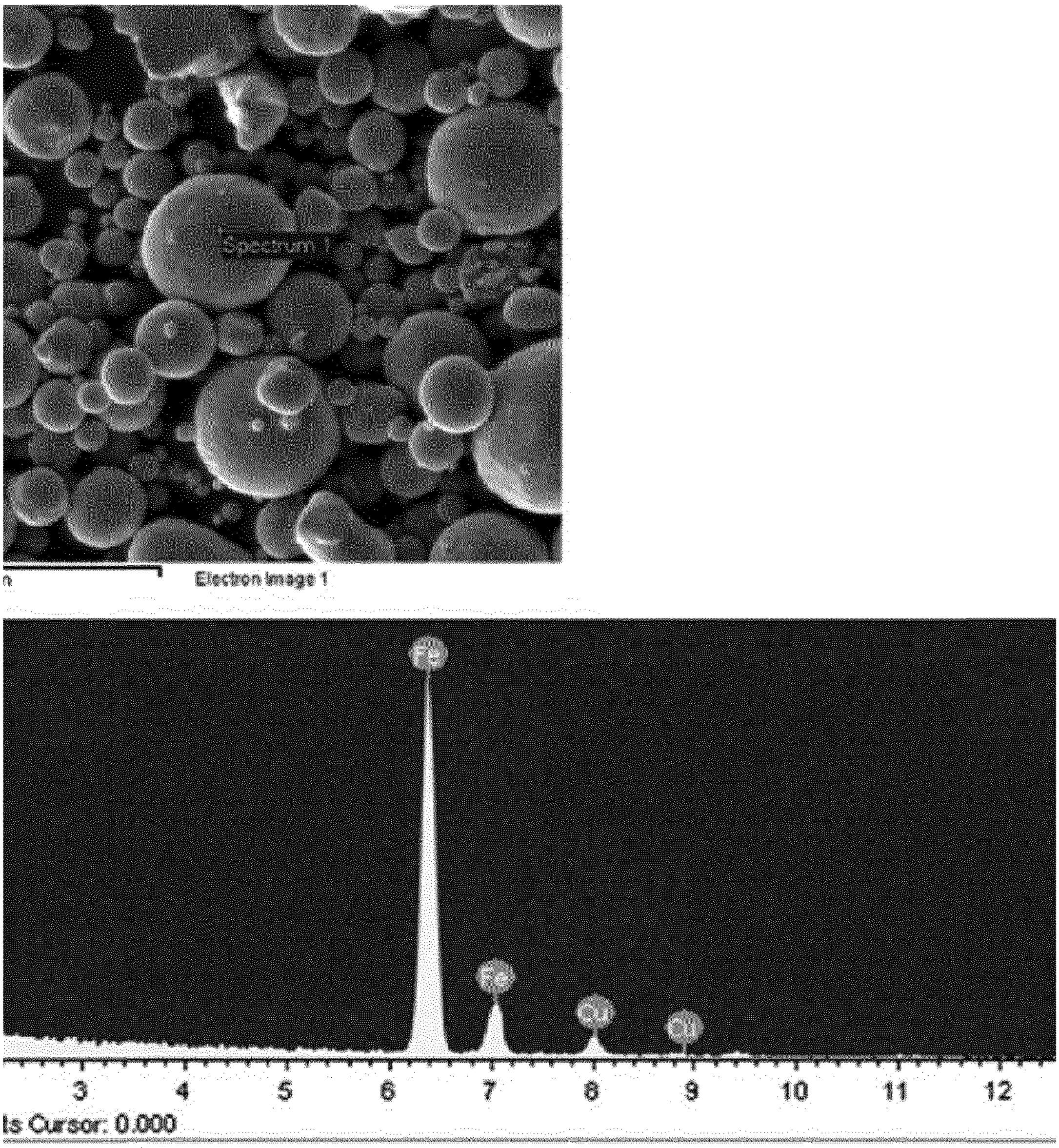
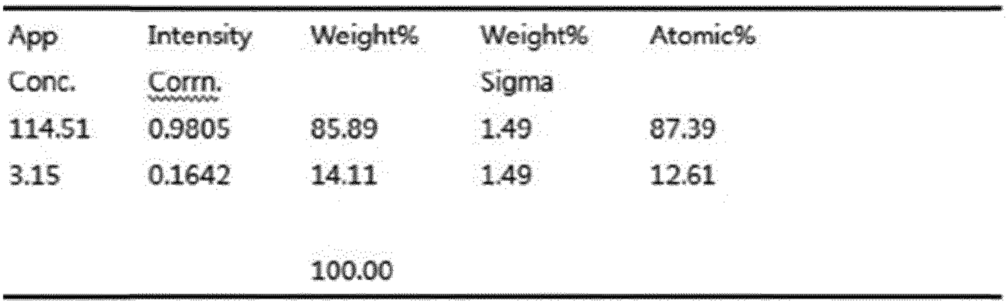


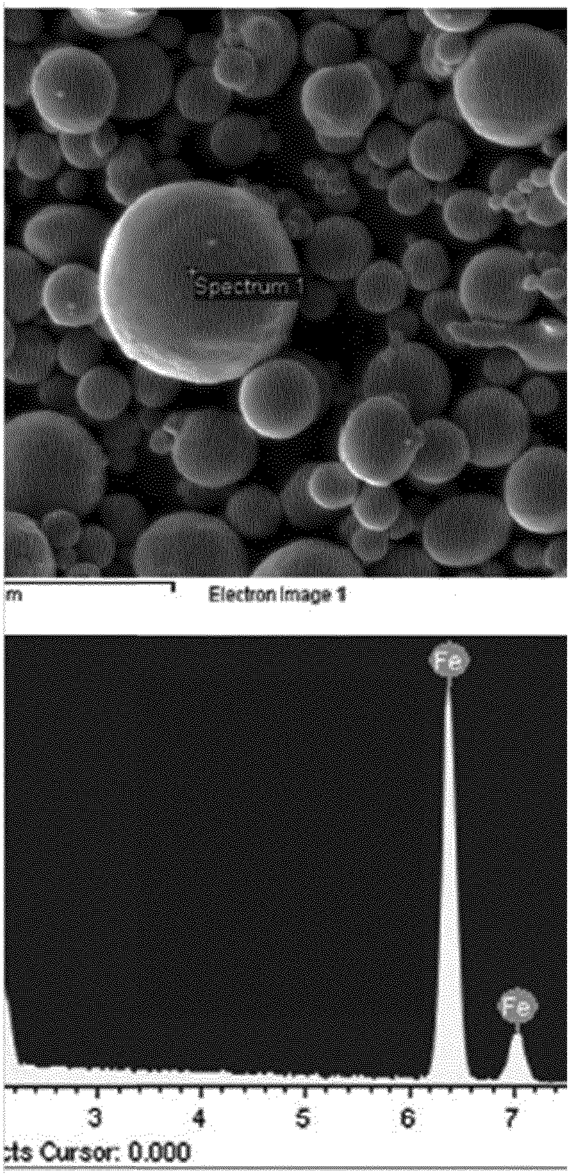
FIG. 4





| App Conc. | Intensity Corrn. | Weight% | Weight% Sigma | Atomic% |
|---|---|---|---|---|
| 114.51 | 0.9805 | 85.89 | 1.49 | 87.39 |
| 3.15 | 0.1642 | 14.11 | 1.49 | 12.61 |
| | | 100.00 | | |

FIG. 5



| App Conc. | Intensity Corrn. | Weight% | Weigh Sigma |
|---|---|---|---|
| 115.81 | 0.9798 | 88.32 | 1.06 |
| 2.50 | 0.1599 | 11.68 | 1.06 |
| | | 100.00 | |

INTERNATIONAL SEARCH REPORT

International application No.
**PCT/KR2017/001262**

A. CLASSIFICATION OF SUBJECT MATTER

*C22C 33/04(2006.01)i, C22C 33/00(2006.01)i, C22C 38/16(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)
C22C 33/04; F27B 14/10; C22F 1/08; C22C 23/00; B22F 9/08; B22D 18/04; C21D 8/00; C22C 1/02; C22C 1/03; C22C 33/00; C22C 38/16

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: iron, copper, alloy, dissolution, molten metal, heating furnace, powder, coating, impurity

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| X | KR 10-2016-0112149 A (DAECHANG CO., LTD.) 28 September 2016<br>See paragraphs [0027]-[0034] and claim 1. | 1,3,8,11,12 |
| Y | | 2,4-7,9,10 |
| Y | KR 10-2013-0078560 A (KOREA INSTITUTE OF MACHINERY & MATERIALS) 10 July 2013<br>See paragraph [0033] and claim 1. | 2,4 |
| Y | JP 2000-282165 A (SHARP CORP. et al.) 10 October 2000<br>See paragraphs [0008], [0009], [0013] and claim 4. | 5-7,9,10 |
| A | JP 05-051712 A (TOSHIBA CORP.) 02 March 1993<br>See paragraph [0046] and claim 1. | 1-12 |
| A | KR 10-2001-0001965 A (KO, Hwa Jin) 05 January 2001<br>See claims 1, 2. | 1-12 |

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

| | | | |
|---|---|---|---|
| * | Special categories of cited documents: | "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 |
| "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 | "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 |
| "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) | "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 |
| "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 | "&" | document member of the same patent family |

| | |
|---|---|
| Date of the actual completion of the international search<br>06 NOVEMBER 2017 (06.11.2017) | Date of mailing of the international search report<br>**07 NOVEMBER 2017 (07.11.2017)** |
| Name and mailing address of the ISA/KR<br>Korean Intellectual Property Office<br>Government Complex-Daejeon, 189 Seonsa-ro, Daejeon 302-701, Republic of Korea<br>Facsimile No. +82-42-481-8578 | Authorized officer<br>Telephone No. |

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

## INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
**PCT/KR2017/001262**

| Patent document cited in search report | Publication date | Patent family member | Publication date |
|---|---|---|---|
| KR 10-2016-0112149 A | 28/09/2016 | NONE | |
| KR 10-2013-0078560 A | 10/07/2013 | KR 10-1334156 B1 | 27/11/2013 |
| JP 2000-282165 A | 10/10/2000 | NONE | |
| JP 05-051712 A | 02/03/1993 | NONE | |
| KR 10-2001-0001965 A | 05/01/2001 | KR 10-0320325 B1 | 10/01/2002 |

Form PCT/ISA/210 (patent family annex) (January 2015)

## REFERENCES CITED IN THE DESCRIPTION

### Patent documents cited in the description

- KR 1020150046014 **[0003]**
- JP 2003003246 A **[0004]**
- KR 1020120048287 **[0004]**
- KR 1020150053814 **[0004]**