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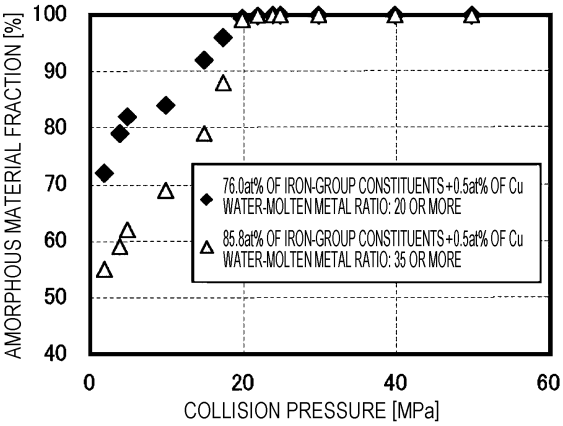
(54) METHOD FOR PRODUCING ATOMIZED METAL POWDER

(57) [Object] Provided is a method for manufacturing atomized metal powder having a high amorphous material fraction by using a water atomizing method.

[Solution] A method for manufacturing atomized metal powder in which atomized metal powder having an amorphous material fraction of 90% or more is obtained, the method including ejecting high-pressure water so as to collide with a molten metal stream flowing vertically downward, separating the molten metal stream into metal powder, and cooling the metal powder, in which the high-pressure water collides with the molten metal with a collision pressure of 20 MPa or higher, and in which a temperature of the molten metal and/or a temperature of the high-pressure water are controlled so that the high-pressure water is in a subcritical state or a supercritical state on a collision surface with the molten metal.

FIG. 4



EP 3 722 028 A1

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Description

Technical Field

[0001] The present invention relates to a method for manufacturing atomized metal powder. In particular, the present invention can preferably be used for manufacturing atomized metal powder containing iron-group constituents (Fe, Ni, and Co) in a total amount of 76 at% or more in terms of atomic fraction.

Background Art

[0002] Conventionally, examples of a method for manufacturing metal powder include an atomizing method. Examples of such an atomizing method include a water atomizing method in which high-pressure water jets (high-pressure water) are ejected to a molten metal stream to obtain metal powder and a gas atomizing method in which an inert gas, instead of water jets, is ejected.

[0003] In a water atomizing method, atomized metal powder is obtained not only by separating a molten metal stream into powdery metal (metal powder) with water jets ejected from, for example, nozzles, but also by cooling the powdery metal (metal powder) with the water jets. On the other hand, in a gas atomizing method, atomized metal powder is usually obtained by dropping powdery metal (metal powder), which has been obtained by separating a molten metal stream into powdery metal with an inert gas ejected through nozzles, into a water tank or a flowing-water drum located under an atomizing apparatus to cool the powdery metal.

[0004] As a method for manufacturing metal powder, a water atomizing method is superior to a gas atomizing method from the viewpoint of high production capability and low cost. In the case of a gas atomizing method, it is necessary to use an inert gas when performing atomizing, and such a method is inferior to a water atomizing method from the viewpoint of atomizing energy. In addition, while metal powder particles manufactured by using a gas atomizing method have an almost spherical shape, metal powder particles manufactured by using a water atomizing method have irregular shapes. Therefore, a water atomizing method has an advantage over a gas atomizing method in that, when metal powder is formed into, for example, a motor core by performing compaction forming, irregularly shaped metal powder particles manufactured by using a water atomizing method are more likely than spherically shaped metal powder particles manufactured by using a gas atomizing method to be entangled with each other to increase strength after compaction has been performed.

[0005] Nowadays, there is a demand for, for example, reducing the iron loss and size of a motor core which is used for an electric automobile or a hybrid automobile from the viewpoint of energy saving. To date, such a motor core has been manufactured by placing thin electrical steel sheets on top of one another. However, nowadays, a motor core manufactured by using metal powder, which has a high degree of freedom for shape design, is receiving much attention. To reduce the iron loss of such a motor core, using non-crystalline (amorphous) metal powder is considered effective. To manufacture amorphous metal powder, it is necessary that atomized metal powder be rapidly cooled by using a coolant to prevent crystallization while atomizing high-temperature molten metal. In addition, it is necessary to increase magnetic flux density to realize a reduction in motor size and an increase in motor power along with a reduction in iron loss. To increase magnetic flux density, increasing iron-group constituent concentration (including Ni and Co) is important, and there is a demand for soft magnetic iron powder, which is an amorphous soft magnetic metal powder for a motor core having an iron-group constituent concentration of about 76 at% to 90 at%. In the case where the iron-group constituent concentration is about 80 at%, it is considered necessary to perform cooling at a cooling rate of 10^6 K/s or more to obtain amorphous metal powder, and it is very difficult to realize both a reduction in iron loss and an increase in magnetic flux density of metal powder at the same time.

[0006] In particular, one of the reasons why an increase in cooling rate is suppressed is as follows. When high-temperature molten metal is cooled with water, since water is instantly vaporized at the time of contact between the water and the molten metal to form vapor films around the molten metal, direct contact between a surface to be cooled and water is suppressed (film boiling occurs), which suppresses an increase in cooling rate.

[0007] To solve the problem of suppressed cooling due to vapor films or film boiling when amorphous iron powder is manufactured, investigations described in Patent Literature 1 through Patent Literature 11 have been conducted.

[0008] For example, Patent Literature 1 describes a method for manufacturing metal powder in which, when molten metal is cooled so as to be solidified when being scattered to obtain metal powder, the cooling rate until the molten metal is solidified is set to be 10^5 K/s or more. It is indicated that, in the case of the technique described in Patent Literature 1, it is possible to achieve the cooling rate described above by bringing the scattered molten metal into contact with a cooling liquid flow which is formed by swirling a cooling liquid along the inner wall surface of a cylinder. In addition, it is indicated that it is preferable that the flow rate of the cooling liquid flow which is formed by swirling the cooling liquid be 5 m/s to 100 m/s.

[0009] In addition, Patent Literature 2 describes a method for manufacturing rapidly solidified metal powder. In the case of the technique described in Patent Literature 2, molten metal is rapidly solidified by feeding the molten metal onto the inner peripheral surface of a swirling cooling liquid layer which is formed by feeding the cooling liquid circumferentially from the outside of the top end of the cylindrical part of a cooling container having a cylindrical inner peripheral surface so that the cooling liquid drops while swirling along the inner peripheral surface of the cylindrical part in such a manner that the swirling cooling liquid layer having a hollow space at the center thereof is centrifugally formed due to swirling. It is indicated that, with this, it is possible to obtain high-quality rapidly solidified powder with high cooling efficiency.

[0010] In addition, Patent Literature 3 describes an apparatus for manufacturing metal powder which uses a gas atomizing method and which has gas jet nozzles for ejecting gas jets onto molten metal flowing downward to separate the molten metal into droplets and a cooling cylinder having an inner peripheral surface along which a cooling liquid layer flows downward while swirling. It is indicated that, in the case of the technique described in Patent Literature 3, it is possible to obtain rapidly solidified fine metal powder as a result of molten metal being separated in two steps consisting of one step utilizing gas-jet nozzles and the other step utilizing a swirling cooling liquid layer.

[0011] In addition, Patent Literature 4 describes a method for manufacturing fine amorphous metal particles in which fine amorphous metal particles are obtained by feeding molten metal into a liquid cooling medium to form vapor films covering the molten metal in the cooling medium and to collapse the formed vapor films so that boiling occurs due to spontaneous nucleation as a result of the molten metal and the cooling medium being brought into direct contact with each other and by utilizing a pressure wave due to boiling to tear the molten metal into pieces so that the molten metal is rapidly cooled to make amorphous metal. It is indicated that it is possible to collapse the vapor films covering the molten metal by controlling the temperature of the molten metal which is fed into the cooling medium so that, when the molten metal and the cooling medium being brought into direct contact with each other, an interface temperature is equal to or lower than a minimum film boiling temperature and equal to or higher than a spontaneous nucleation temperature or by performing ultrasonic irradiation.

[0012] In addition, Patent Literature 5 describes a method for manufacturing fine particles in which a molten material is made into fine particles and cooled so as to be solidified by controlling the temperature of the molten material so that the material is molten at a temperature equal to or higher than the spontaneous nucleation temperature of a cooling liquid medium when the molten material is fed into the cooling liquid medium in the form of droplets or jets and by controlling a relative velocity between the molten material and the cooling liquid medium when the molten material is fed into the cooling liquid medium to be 10 m/s or more to forcibly collapse vapor films formed around the molten material so that boiling occurs due to spontaneous nucleation. It is indicated that, with this, it is possible to manufacture fine particles or an amorphous material from a material which is difficult to make into fine particles or an amorphous material by using conventional methods.

[0013] In addition, Patent Literature 6 describes a method for manufacturing a functional member which has a process of obtaining homogeneous functional fine particles of polycrystalline or amorphous material without segregation by dissolving a raw material to which a functional additive is added in a base material and by feeding the molten mixture into a cooling liquid medium so that the molten mixture is made into fine particles due to vapor explosion and cooled so as to be solidified while controlling the cooling rate and a process of obtaining a functional member by compressing the functional fine particles and fine particles of the base material used as raw materials.

[0014] Patent Literature 7 and Patent Literature 8 state that it is possible to collapse vapor films formed around powder particles, which have been obtained by atomizing a molten material, by suctioning the particles into a suction pipe disposed below a water atomizing device.

[0015] Patent Literature 9 states that vapor films formed around powder particles, which have been obtained by atomizing a molten material, are collapsed by ejecting a liquid at a pressure of 80 kgf/cm^2 or higher so that the particles collide with a cooling block disposed below a water atomizing device.

[0016] Patent Literature 10 states that covering vapor films are removed by ejecting a second liquid from a device for ejecting the second liquid, which is disposed below an atomizing device, at an ejection pressure of the liquid of 5 MPa to 20 MPa to forcibly change the moving direction of a fluid dispersion containing molten metal.

[0017] Patent Literature 11 discloses an invention regarding an iron-boron-based ferromagnetic material (permanent magnet) containing a rare-earth metal and states that, when performing pulverizing and manufacturing of an amorphous material by using a water atomizing method, it is preferable that a water pressure be 750 kgf/cm^2 to 1200 kgf/cm^2, that a water temperature be 20°C or lower, and that the amount (kg) of water for 1 kg of iron be 25 [-] to 45 [-].

Citation List

Patent Literature

[0018]

PTL 1: Japanese Unexamined Patent Application Publication No. 2010-150587

PTL 2: Japanese Examined Patent Application Publication No. 7-107167
PTL 3: Japanese Patent No. 3932573
PTL 4: Japanese Patent No. 3461344
PTL 5: Japanese Patent No. 4793872
PTL 6: Japanese Patent No. 4784990
PTL 7: Japanese Unexamined Patent Application Publication No. 60-24302
PTL 8: Japanese Unexamined Patent Application Publication No. 61-204305
PTL 9: Japanese Unexamined Patent Application Publication No. 60-24303
PTL 10: Japanese Unexamined Patent Application Publication No. 2007-291454
PTL 11: Japanese Unexamined Patent Application Publication No. 2004-349364

Summary of Invention

Technical Problem

[0019] In the case of the techniques described in Patent Literature 1 through Patent Literature 3, it is intended to remove vapor films formed around separated metal particles by feeding molten metal into a cooling liquid layer formed by swirling the cooling liquid. However, in the case where the temperature of the separated metal particles is high, since film boiling tends to occur in the cooling liquid layer, and since the metal particles fed into the cooling liquid layer move along with the cooling liquid layer, that is, a relative velocity with respect to the cooling liquid layer is small, there is a problem in that it is difficult to avoid film boiling.

[0020] In addition, in the case of the techniques described in Patent Literature 1 through Patent Literature 6, since a gas atomizing method is used to manufacture metal powder, and since it is necessary to use a large amount of inert gas for atomizing in a gas atomizing method, there is a problem of an increase in manufacturing costs.

[0021] The techniques described in Patent Literature 7 through Patent Literature 10 relate to a water atomizing method. In the case of the techniques described in Patent Literature 7 and Patent Literature 8, it is indicated that it is possible to remove vapor films by suctioning powder. However, when water exists around a high-temperature object, since water is continuously vaporized to form vapor films due to heat fed from the inside of the object, the water and the molten metal are suctioned together with no change, and it is difficult to remove the vapor films.

[0022] Patent Literature 9 states that it is possible to collapse vapor films by allowing molten metal which is covered with vapor films to collide with a cooling block disposed below an atomizing device. However, in the case where a liquid is used for separation, since there is an increase in the temperature of the liquid, vapor films tend to be formed. In addition, since the ejection pressure (pressure energy) of the liquid is utilized for separation, there is insufficient energy for collapsing vapor films at the time of collision with the cooling block. Even if vapor films are collapsed, vapor films soon re-form as long as the molten metal (powder) has a high temperature. Therefore, it is necessary to always continue removing vapor films.

[0023] In addition, Patent Literature 10 states that, it is possible to remove vapor films by changing the moving direction of a liquid dispersion containing molten metal droplets, which have been formed by performing atomizing, by using a liquid jet spray. However, in the case where the temperature of the molten metal covered with vapor films is excessively high when the moving direction is changed, the molten metal may be covered with vapor films again due to surrounding cooling water. On the contrary, in the case where the temperature of the molten metal is excessively low when the molten metal collides with a cooling block, there may be a case where the molten metal solidifies and crystallization progresses. In particular, in the case where the content of iron-group elements (Fe + Co + Ni) is large, since there is an increase in cooling start temperature due to an increase in melting point, film boiling tends to occur at the beginning of cooling. Therefore, it may be said that an ejection pressure of a liquid of about 5 MPa to 20 MPa is not sufficient.

[0024] Patent Literature 11 relates to powder for a permanent magnet and states that, to make powder pulverized and amorphous, water pressure is set to be 750 kgf/cm^2 to 1200 kgf/cm^2, water temperature is set to be 20°C or lower, and the amount of water for 1 kg of iron is set to be 25 L (liters) to 45 L. Although it is not indicated that film boiling or a vapor film is eliminated under these conditions, controlling an ejection pressure to be 60 MPa or higher incurs costs for a high-pressure pump and high-pressure pipework, which results in an increase in product price. In addition, although the amount of water for 1 kg of iron is set to be 25 L to 45 L, it may be said that this amount is not sufficient for a soft magnetic material having a high iron-group constituent content.

[0025] As described above in Background Art, a water atomizing method is advantageous from the viewpoint of productivity and the adhesiveness of particles. In addition, when rapid cooling is performed to manufacture an amorphous material, performing rapid cooling with water after having performed gas atomizing is advantageous for the manufacture of an amorphous material as in the case of Patent Literature 1 through Patent Literature 6. In the case of a water atomizing method, since molten metal separated by performing atomizing is covered with vapor films due to cooling water that is used for atomizing, it is necessary to take further measures exemplified by those described in Patent Literature 7 through

Patent Literature 11. In particular, in the case of such measures, there is an insufficient effect for manufacturing an amorphous soft magnetic material containing iron-group elements in a total amount of 76 at% or more.

[0026] The present invention has been completed to solve the problems described above, and an object of the present invention is to provide a method for manufacturing atomized metal powder having a high amorphous material fraction by using a water atomizing method.

Solution to Problem

[0027] The present inventors diligently conducted investigations to solve the problems described above and, as a result, solved the problems by focusing on collision pressure instead of ejection pressure when atomized metal powder is obtained by ejecting high-pressure water onto molten metal to separate and cool the molten metal and by controlling the state of water on the collision surface between the molten metal and the high-pressure water. More specifically, the present invention provides the following.

[1] A method for manufacturing atomized metal powder in which atomized metal powder having an amorphous material fraction of 90% or more is obtained, the method including ejecting high-pressure water so as to collide with a molten metal stream flowing vertically downward, separating the molten metal stream into metal powder, and cooling the metal powder,
in which the high-pressure water collides with the molten metal with a collision pressure of 20 MPa or higher, and in which a temperature of the molten metal and/or a temperature of the high-pressure water are controlled so that the high-pressure water is in a subcritical state or a supercritical state on a collision surface with the molten metal.
[2] The method for manufacturing atomized metal powder according to item [1], in which an average temperature of the molten metal and the high-pressure water is 374°C or higher at a time of collision between the high-pressure water and the molten metal.
[3] The method for manufacturing atomized metal powder according to item [1] or [2], in which, when a flow rate of the molten metal stream per unit time is defined as Qm (kg/min) and an ejection rate of the high-pressure water per unit time is defined as Qaq (kg/min), a mass ratio (Qaq/Qm) is 35 or more.
[4] The method for manufacturing atomized metal powder according to any one of items [1] to [3], in which the atomized metal powder contains iron-group constituents (Fe, Ni, and Co) in a total amount of 76.0 at% or more in terms of atomic fraction and Cu in an amount of 0.1 at% or more and 2.0 at% or less in terms of atomic fraction.
[5] The method for manufacturing atomized metal powder according to any one of items [1] to [3], in which the atomized metal powder contains iron-group constituents (Fe, Ni, and Co) in a total amount of more than 82.5 at% and less than 86 at% in terms of atomic fraction, at least two selected from Si, P, and B, and Cu and has an average particle size of 5 μm or more.
[6] The method for manufacturing atomized metal powder according to any one of items [1] to [5], in which the subcritical state is represented by a pressure of 0.5 MPa to 22 MPa and a water temperature of 150°C to 274°C, and in which the supercritical state is represented by a pressure of 22 MPa or higher and a water temperature of 374°C or higher.

Advantageous Effects of Invention

[0028] According to the present invention, it is possible to manufacture atomized metal powder having an amorphous material fraction of 90% or more. With this, by performing an appropriate heat treatment after having performed forming on the atomized metal powder obtained by using the present invention, nanosized crystals are precipitated. In particular, in the case where such powder is made of a soft magnetic material having a high iron-group constituent content (containing iron-group constituents (Fe, Ni, and Co) in a total amount of 76 at% or more in terms of atomic fraction), by performing an appropriate heat treatment after having performed forming on such powder, it is possible to achieve both low iron loss and high magnetic flux density. In such a manner, the present invention can preferably be used for manufacturing any conventionally known amorphous soft magnetic material.

[0029] Nowadays, in addition, as described in, for example, Materia Japan, Vol. 41, No. 6, p. 392, the Journal of Applied Physics 105, 013922 (2009), Japanese Patent No. 4288687, Japanese Patent No. 4310480, Japanese Patent No. 4815014, International Publication No. WO2010/084900, Japanese Unexamined Patent Application Publication No. 2008-231534, Japanese Unexamined Patent Application Publication No. 2008-231533, and Japanese Patent No. 2710938, hetero-amorphous materials and nanocrystalline materials having a high magnetic flux density have been developed. The present invention can very advantageously be used when such a soft magnetic material having a high iron-group constituent concentration is manufactured by using a water atomizing method. In particular, in the case where the iron-group constituent concentration is more than 82.5 at%, or further, more than 83.5 at%, it was difficult to increase an amorphous material fraction by using conventional techniques. However, by using the manufacturing method according to the present invention, it is possible to increase the amorphous material fraction to 90% or more after atomizing has been performed. Moreover, it was very difficult to control the amorphous material fraction to be 90% or more and an average particle size to be 5 μm or more by using conventional techniques. However, by using the manufacturing method according to the present invention, it is possible to control the amorphous material fraction to be 90% or more, even in the case where the average particle size is increased. Since it is possible to control the amorphous material fraction to be 90% or more and the average particle size to be 5 μm or more, there is a significant increase in saturated magnetic flux density (Bs) by performing an appropriate heat treatment after having performed forming on atomized metal powder.

[0030] In addition, although the present invention can preferably be used to manufacturing atomized metal powder having a high iron-group constituent concentration as described above, by using the present invention as a method for manufacturing atomized metal powder other than that having a high iron-group constituent concentration, there is an advantage in that it is possible to stably obtain amorphous powder having a high particle size more easily than before.

[0031] Here, the term "amorphous material fraction" denotes a value obtained by removing contaminants which are different from metal powder from the obtained metal powder (soft magnetic iron powder), by performing X-ray diffractometry to determine halo peaks from amorphous materials (non-crystalline materials) and diffraction peaks from crystals, and by performing a calculation by utilizing a WPPD method. The term "WPPD method" here is an abbreviation of "whole-powder-pattern decomposition method". The WPPD method is described in detail in Hideo Toraya: Journal of the Crystallographic Society of Japan, vol. 30 (1988), No. 4, pp. 253 to 258.

Brief Description of Drawings

[0032]

[Fig. 1] Fig. 1 is a schematic diagram of an example of a manufacturing apparatus which can be used in a method for manufacturing atomized metal powder according to the present invention.

[Fig. 2] Fig. 2 is a schematic diagram illustrating an example of manufacturing equipment for implementing the manufacturing method according to the present invention.

[Fig. 3] Fig. 3 is a diagram illustrating the relationship between the pressure, temperature, and state of water.

[Fig. 4] Fig. 4 is a graph illustrating the relationship between an amorphous material fraction and a collision pressure.

[Fig. 5] Fig. 5 is a schematic diagram illustrating a measurement configuration for determining the collision pressure of molten metal by using a collision pressure sensor.

[Fig. 6] Fig. 6 is a diagram illustrating a B-H diagram obtained by using a VSM.

Description of Embodiments

[0033] Hereafter, an embodiment of the present invention will be described. Here, the present invention is not limited to the embodiment below.

[0034] Fig. 1 schematically illustrates an example of a manufacturing apparatus which can be used in a method for manufacturing atomized metal powder according to the present invention. In Fig. 1, after molten metal 3 has been charged into a tundish 2, the molten metal 3 flows downward through a molten metal-injecting nozzle 4 due to the weight of the molten metal 3. In addition, cooling water 20 (corresponding to high-pressure water) fed into a nozzle header 5 is ejected through cooling nozzles 6. The cooling water 20 collides with the molten metal (molten metal stream flowing downward) and, as a result, the molten metal is atomized, that is, separated into metal powder 8.

[0035] Fig. 2 schematically illustrates an example of manufacturing equipment for implementing the manufacturing method according to the present invention. In the manufacturing equipment illustrated in Fig. 2, atomized metal powder is manufactured by controlling the temperature of cooling water in a cooling water tank 15 by using a cooling water-temperature controller 16, by transporting the cooling water, whose temperature has been controlled, to a high-pressure pump 17 for atomizing cooling water, by transporting the cooling water from the high-pressure pump 17 for atomizing cooling water through pipework 18 for atomizing cooling water to an atomizing apparatus 14 (corresponding to the manufacturing apparatus in Fig. 1), and by ejecting the high-pressure water, which collides with the molten metal stream flowing vertically downward, from this atomizing apparatus 14 to separate the molten metal stream into metal powder and to cool the metal powder.

[0036] First, the present invention is characterized by controlling a collision pressure to be 20 MPa or higher when the cooling water 20 collides with the molten metal and the state of the water to be a subcritical state of water or a supercritical state of water on a collision surface. The expression "supercritical state of water" denotes a state which is represented by a temperature of 374°C or higher and a pressure of 22 MPa or higher. The expression "subcritical state of water" denotes a high-temperature and high-pressure state which is close to a critical point and which is exemplified by, as illustrated in Fig. 3, a state which is represented by a temperature of 100°C or higher and lower than 374°C and a pressure of 0.1 MPa or higher and lower than 22 MPa, a state which is represented by a temperature of 374°C or higher and a pressure of 2 MPa or higher and lower than 22 MPa, and a state which is represented by a temperature of 250°C or higher and lower than 374°C and a pressure of 22 MPa or higher.

[0037] In the manufacturing method according to the present invention, the collision pressure of the cooling water 20 at the time of collision with the molten metal is set to be 20 MPa or more. The collision pressure is determined by using a pressure sensor having a collision surface sensor whose diameter is 2 mm when atomizing is not performed. To control the collision pressure to be 20 MPa or more, it is necessary that the ejection pressure of the cooling water 20 be more than the collision pressure. To control the collision pressure so that the maximum ejection pressure is 98 MPa, it is preferable that the pressure control be performed by using an inverter high-pressure pump. In addition, since there is a decrease in ejection pressure in the case where the cooling water 20 is spread out in a fan-like form, it is preferable that solid stream-type nozzles be used. In addition, since there is a decrease in ejection pressure in the case where the distance between the cooling nozzles 6 and the molten metal is increased, it is preferable that the linear distance between the ejection ports of the cooling nozzles 6 for the cooling water 20 and the molten metal be 150 mm or less or more preferably 100 mm or less.

[0038] In addition, in the present invention, the temperature of the molten metal and/or the temperature of the cooling water are controlled so that the cooling water 20 is in a subcritical state or a supercritical state on a collision surface with the molten metal. It is possible to control the temperature of the molten metal by controlling the heating temperature of a melting furnace through highfrequency output. In addition, by holding the molten metal 3 in the melting furnace after heating has been performed, it is possible to control the temperature of the molten metal 3 which is fed into the tundish 2.

[0039] In the manufacturing method according to the present invention, the temperature of the water on the collision surface is defined as the average temperature of the molten metal and the cooling water 20 (((molten metal temperature) + (cooling water temperature))/2). It is possible to determine the molten metal temperature by using a non-contact thermometer at an atomizing point. It is possible to determine the temperature of the cooling water by using a thermometer (not illustrated) for determining the water temperature in the cooling water tank 15 illustrated in Fig. 2. In addition, in accordance with the relationship between the pressure, the temperature, and the state of water illustrated in Fig. 3, the collision pressure, the temperature of the molten metal, and the temperature of the cooling water 20 are controlled to achieve the average temperature and the collision pressure with which the cooling water is in a subcritical state or a supercritical state. Here, since the temperatures of the molten metal and the cooling water tend to fluctuate, the molten metal temperature may be determined within the margin of error of plus or minus 50°C, and the cooling water temperature may be determined within the margin of error of plus or minus 5°C.

[0040] Hereafter, the effects of the present invention will be described.

[0041] Fig. 4 is a graph illustrating the relationship between an amorphous material fraction and a collision pressure. The graph in Fig. 4 relates to a case where atomized metal powder containing iron-group constituents (Fe, Ni, and Co) in a total amount of 76.0 at% in terms of atomic fraction (water-molten metal ratio(mass ratio: Qaq/Qm): 20) and Cu in an amount of 0.5 at% is manufactured and a case where atomized metal powder containing iron-group constituents (Fe, Ni, and Co) in a total amount of 85.8 at% in terms of atomic fraction (water-molten metal ratio: 35) and Cu in an amount of 0.5 at% is manufactured. In addition, in the graph in Fig. 4, in the case of a collision pressure of 20 MPa, the state of water was controlled to be a subcritical state on the collision surface between the cooling water and the molten metal. In the case of a collision pressure of 22 MPa or higher, that is, in the case of a collision pressure of higher than 20 MPa, the state of water was controlled to be a supercritical state on the collision surface between the cooling water and the molten metal. In addition, in the case of a collision pressure of lower than 20 MPa, the state of water was controlled not to be either a subcritical state or a supercritical state on the collision surface between the cooling water and the molten metal.

[0042] As indicated in Fig. 4, in the case where the collision pressure is 20 MPa or higher, it is possible to achieve an amorphous material fraction of 90% or more regardless of a variation in the chemical composition of obtained atomized metal powder, a variation in water-molten metal ratio, or whether the state of the water is a subcritical state or a supercritical state on a collision surface.

[0043] In addition, when the manufacturing method according to the present invention is implemented, it is preferable that the average temperature of the molten metal and the cooling water be 374°C or higher at the time of collision between the cooling water (high-pressure water) and the molten metal. By controlling the average temperature described above to be 374°C or higher, there is an advantage in that the state of water is brought close to a critical state and that there is an increase in vapor density.

[0044] When the flow rate of the molten metal stream per unit time is defined as Qm (kg/min) and the ejection rate of the cooling water (high-pressure water) per unit time is defined as Qaq (kg/min), it is preferable that a mass ratio (Qaq/Qm) be 35 or more. This is because, since there is a tendency for an amorphous material fraction to increase in the case where such a mass ratio is large, and since it is easy to control the mass ratio in the case where the mass ratio is 35 or more, it is possible to achieve a sufficiently high level of effect.

[0045] The manufacturing method according to the present invention can preferably be used for manufacturing atomized metal powder containing iron-group constituents (Fe, Ni, and Co) in a total amount of 76 at% or more in terms of atomic fraction and Cu in an amount of 0.1 at% or more and 2 at% or less in terms of atomic fraction. In the case where the content of iron-group elements (Fe + Co + Ni) is large, since there is an increase in cooling start temperature due to an increase in melting point, film boiling tends to occur at the beginning of cooling, which makes it difficult to increase an amorphous material fraction to 90% or more by using conventional methods. According to the present invention, it is possible to increase an amorphous material fraction, even in the case where the content of iron-group elements (Fe + Co + Ni) is large. By using the manufacturing method according to the present invention, since it is possible to increase an amorphous material fraction while increasing the content of iron-group elements (Fe + Co + Ni), it is possible to increase magnetic flux density. As a result, the manufacturing method according to the present invention contributes to reducing the size of a motor and to increasing motor power.

[0046] Here, by controlling the chemical composition of the molten metal to be within the range described above, the chemical composition of the atomized metal powder is also within the range described above.

[0047] The manufacturing method according to the present invention can preferably be used for manufacturing atomized metal powder containing iron-group constituents (Fe, Ni, and Co) in a total amount of more than 82.5 at% and less than 86.0 at% in terms of atomic fraction, at least two selected from Si, P, and B, and Cu and having an average particle size of 5 μm or more. In the case where conventional techniques are used for manufacturing atomized metal powder containing iron-group constituents in significantly large amounts, specifically, containing iron-group constituents (Fe, Ni, and Co) in a total amount of more than 82.5 at% and less than 86 at% in terms of atomic fraction, when an average particle size is small, since it is easy to cool the particles, it is possible to achieve an amorphous material fraction larger than that achieved when the average particle size is large. However, when the average particle size is 5 μm or more, it is very difficult to increase the amorphous material fraction to 90% or more. According to the present invention, even when the average particle size is 5 μm or more, it is possible to increase the amorphous material fraction to 90% or more. In addition, the upper limit of the average grain diameter with which it is possible to increase the amorphous material fraction to 90% or more by using the present invention is 75 μm as a rough guide. Here, the particle size is determined by performing classification utilizing a sieve method, and the average particle size (D50) is calculated by using an integration method. In addition, a laser diffraction/scattering particle size distribution analyzer may also be used.

EXAMPLES

[0048] Examples and comparative examples were implemented by using the manufacturing equipment illustrated in Fig. 2 in which the apparatus for manufacturing water-atomized metal powder illustrated in Fig. 1 was installed.

[0049] Molten metal 3, which has been prepared by melting a raw material at a predetermined temperature by using a highfrequency melting furnace or the like, is fed into a tundish 2. A molten metal-injecting nozzle 4 having a predetermined molten metal-injecting nozzle diameter has been set in the tundish 2 in advance. When the molten metal 3 is fed into the tundish 2, the molten metal is extruded through the molten metal-injecting nozzle 4 due to free drop or back pressure and flows downward. Cooling water, which is ejected through cooling water nozzles 6 with a predetermined water pressure by using a high-pressure pump 17 for atomizing cooling water, collides with the molten metal, so that the molten metal is separated, pulverized, and cooled. There may be a case where the cooling water has been stored in a cooling water tank 15 in advance to control the water temperature by using a cooling water-temperature controller 16 as needed. As the cooling water ejecting nozzles, solid stream-type nozzles were used. A dozen cooling water nozzles were arranged around the molten metal flowing downward so as to make an angle of 30° with respect to the vertical direction. Here, it is possible to realize the effects of the present invention, even in the case where the nozzles are arranged so as to make an angle of 5° to 60° with respect to the vertical direction. Before atomizing is started, the collision pressure of the molten metal is determined by using a collision pressure sensor 51 (refer to Fig. 5). The collision pressure sensor 51 is arranged in a direction perpendicular to the nozzle ejection direction to confirm whether a predetermined collision pressure is achieved. Here, although Fig. 5 illustrates not only a configuration in which the cooling water is ejected onto the molten metal but also a configuration in which the cooling water is ejected onto the collision pressure sensor 51, this is only for the purpose of description, and the collision pressure is determined by using the collision pressure sensor 51 before the molten metal is allowed to flow down. Iron powder manufactured from the molten metal is collected by using a hopper, dried, classified, and subjected to evaluation regarding an amorphous material fraction. In the case of an amorphous material fraction of 90% or more is judged as satisfactory.

[0050] When the manufacturing methods of the examples and the comparative examples were implemented, soft magnetic materials having the following chemical compositions were prepared. "%" means "at%". (i) through (v) are Fe-based soft magnetic row materials. (vi) is an Fe-Co-based soft magnetic material. (vii) is an Fe-Co-Ni-based soft magnetic material.

(i) Fe76%-Si9%-B10%-P5%
(ii) Fe78%-Si9%-B9%-P4%

(iii) Fe80%-Si8%-B8%-P4%
(iv) Fe82.8%-B11%-P5%-Cu1.2%
(v) Fe84.8%-Si4%-B10%-Cu1.2%
(vi) Fe69.8%-Co15%-B10%-P4%-Cu1.2%
(vii) Fe69.8%-Ni1.2%-Co15%-B9.4%-P3.4%-Cu1.2%

[0051] Although (i) through (vii) were prepared so that each of the materials had a corresponding one of the target chemical compositions, in actual chemical compositions, after having performed melting and atomizing, there were errors within the margin of about plus or minus 0.3 at% or impurities were contained in some cases. In addition, in some cases, there was some variation in chemical composition due to, for example, oxidation occurring in a melting process or an atomizing process or after an atomizing process.

[0052] Examples 1 through 4 and comparative examples 1 through 3 were implemented under the conditions given in Table 1. The average particle size and the amorphous material fraction were evaluated by using the method described above. From the results of the examples and the comparative examples, it was clarified that an amorphous material fraction of 90% or more was achieved in the case of all the examples, which were within the range of the present invention. In the case of the comparative examples, an amorphous material fraction of 90% or more was not achieved.

[0053] The atomized metal powder of examples 1 through 4 were subjected to an appropriate heat treatment after having been subjected to forming. With this, nanosized crystals were precipitated. In addition, it was clarified that both low iron loss and high magnetic flux density were achieved. Specifically, such results were clarified by using the following method.

[0054] The sizes of the nanosized crystals were derived by using the Scherrer equation after having performed determination utilizing an XRD (X-ray diffractometer). In the Scherrer equation, K denotes a shape factor (usually assigned a value of 0.9), β denotes a full-width at half maximum (expressed in units of radian), θ is expressed by the equation $2\theta = 52.505°$ (Fe110-plane), and τ denotes a crystal size.

$$\tau = K\lambda/\beta\cos\theta \quad \text{(Scherrer equation)}$$

[0055] In addition, the magnetic properties of the obtained powder were investigated by using a VSM (vibrating sample magnetometer), and, from the B-H diagram (Fig. 6) obtained by using the VSM, the saturated magnetic flux density was determined from point C (point F), the retaining force was determined from point E, the magnetic permeability was determined from the maximum slope of B, and the iron loss was determined from the hysteresis area (C-D-F-G). Here, the diagram in Fig. 6 is opened to the public by Japan Science and Technology Agency (JST), which is one of the National Research and Development Agencies, (URL: https://www.jst.go.jp/pr/report/report27/grf2.html, as searched on 16th November 2017)

[Table 1]

Example/ Comparative Example	Molten Metal Flow (Downward) Rate [kg/min]	Cooling Water Flow Rate [kg/min]	Water-Molten Metal Ratio [-]	Temperature of High-pressure Water [°C]	Ejection Pressure of High-pressure Water [MPa]	Collision Pressure [MPa]	Atomizing Start Temperature [°C]	Average Temperature [°C]	State of Water	Chemical Composition [at%]	Iron-group Constituent	Average Particle Size [μm]	Amorphous Material Fraction [%]	Judgement
											Fe+Ni+Co [at%]			(A ratio of 90% or more is satisfactory.)
Example 1	15	300	20	10	90	20	1200	605	Subcritical	(i) $Fe_{76}Si_9B_{10}P_5$	76.0	32	93	Satisfactory
Example 2	15	420	28	10	90	20	1200	605	Subcritical	(i) $Fe_{76}Si_9B_{10}P_5$	76.0	33	99	Satisfactory
				10	90			605	Subcritical	(ii) $Fe_{78}Si_9B_9P_4$	78.0	33	97	Satisfactory
				10	90			605	Subcritical	(iii) $Fe_8oSi_8BsP_4$	80.0	35	94	Satisfactory
Example 3	12	420	35	10	100	23	1200	605	Supercritical	(i) $Fe_{76}Si_9B_{10}P_5$	76.0	34	100	Satisfactory
				10	100			605	Supercritical	(ii) $Fe_{78}Si_9B_9P_4$	78.0	29	99	Satisfactory
				10	100			605	Supercritical	(iii) $Fe_8oSi_8BsP_4$	80.0	29	97	Satisfactory
				10	100			605	Supercritical	(iv) $Fe_{82.8}B_{11}P_5Cu_{1.2}$	82.8	35	95	Satisfactory
				10	100			605	Supercritical	(v) $Fe_{84.8}Si_4B_{10}Cu_{1.2}$	84.8	36	94	Satisfactory
				10	100			605	Supercritical	(vi) $Fe_{69.8}Co_{15}B_{10}P_4Cu_{1.2}$	84.8	32	93	Satisfactory
				10	100			605	Supercritical	(vii) $Fe_{69.8}Ni_{1.2}Co_{15}B_{9.4}P_{3.4}Cu_{1.2}$	86.0	35	92	Satisfactory

(continued)

Example/ Comparative Example	Molten Metal Flow (Downward) Rate [kg/min]	Cooling Water Flow Rate [kg/min]	Water-Molten Metal Ratio [-]	Temperature of High-pressure Water [°C]	Ejection Pressure of High-pressure Water [MPa]	Collision Pressure [MPa]	Atomizing Start Temperature [°C]	Average Temperature [°C]	State of Water	Chemical Composition [at%]	Iron-group Constituent	Average Particle Size [μm]	Amorphous Material Fraction [%]	Judgement
											Fe+Ni+Co [at%]			(A ratio of 90% or more is satisfactory.)
Comparative Example 1	12	120	8	10	55	12	1200	605	Vapor	(i) $Fe_{76}Si_9B_{10}P_5$	76.0	43	83	Unsatisfactory
				10	55			605	Vapor	(ii) $Fe_{78}Si_9B_9P_4$	78.0	44	62	Unsatisfactory
				10	55			605	Vapor	(iii) $Fe_8oSi_8BsP_4$	80.0	43	45	Unsatisfactory
				10	55			605	Vapor	(iv) $Fe_{82.8}B_{11}P_5Cu_{1.2}$	82.8	44	40	Unsatisfactory
				10	55			605	Vapor	(v) $Fe_{84.8}Si_4B_{10}Cu_{1.2}$	84.8	45	38	Unsatisfactory
				10	55			605	Vapor	(vi) $Fe_{69.8}Co_{15}B_{10}P_4Cu_{1.2}$	84.8	42	35	Unsatisfactory
				10	55			605	Vapor	(vii) $Fe_{69.8}Ni_{1.2}Co_{15}B_{9.4}P_{3.4}Cu_{1.2}$	86.0	39	32	Unsatisfactory

(continued)

Example/ Comparative Example	Molten Metal Flow (Downward) Rate [kg/min]	Cooling Water Flow Rate [kg/min]	Water-Molten Metal Ratio [-]	Temperature of High-pressure Water [°C]	Ejection Pressure of High-pressure Water [MPa]	Collision Pressure [MPa]	Atomizing Start Temperature [°C]	Average Temperature [°C]	State of Water	Chemical Composition [at%]	Iron-group Constituent	Average Particle Size [μm]	Amorphous Material Fraction [%]	Judgement
											Fe+Ni+Co [at%]			(A ratio of 90% or more is satisfactory.)
Comparative Example 2	12	420	35	10	60	15	1200	605	Vapor	(i) $Fe_{76}Si_9B_{10}P_5$	76.0	44	88	Unsatisfactory
				10	60			605	Vapor	(ii) $Fe_{78}Si_9B_9P_4$	78.0	42	73	Unsatisfactory
				10	60			605	Vapor	(iii) $Fe_8oSi_8BsP_4$	80.0	39	63	Unsatisfactory
				10	60			605	Vapor	(vi) $Fe_{82.8}B_{11}P_5Cu_{1.2}$	82.8	43	53	Unsatisfactory
				10	60			605	Vapor	(v) $Fe_{84.8}Si_4B_{10}Cu_{1.2}$	84.8	46	52	Unsatisfactory
				10	60			605	Vapor	(vi) $Fe_{69.8}Co_{15}B_{10}P_4Cu_{1.2}$	84.8	43	46	Unsatisfactory
				10	60			605	Vapor	(vii) $Fe_{69.8}Ni_{1.2}Co_{15}B_{9.4}P_{3.4}Cu_{1.2}$	86.0	43	44	Unsatisfactory
Comparative Example 3	10	350	35	10	15	5	1200	605	Vapor	(i) $Fe_{76}Si_9B_{10}P_5$	76.0	38	5	Unsatisfactory
Example 4	12	480	40	10	90	20	1200	605	Subcritical	(i) $Fe_{76}Si_9B_{10}P_5$	76.0	33	100	Satisfactory

[0056] In Table 1, the term "Atomizing Start Temperature" denotes the temperature of the molten metal at the atomizing point. The temperature of the molten metal at the atomizing point was determined by using a non-contact thermometer.

[0057] In Table 1, the term "Average Temperature" denotes a value obtained by using the formula ((molten metal temperature) + (cooling water temperature))/2. The molten metal temperature at the atomizing point was determined by using a non-contact thermometer at an atomizing point, and the cooling water temperature was defined as the temperature of water in the cooling water tank which was determined by using a thermometer.

[0058] In Table 1, the term "Water-Molten Metal Ratio" denotes the mass ratio Qaq/Qm.

Reference Signs List

[0059]

2	tundish
3	molten metal
4	molten metal-injecting nozzle
5	nozzle header
6	cooling nozzle
8	metal powder
14	atomizing apparatus
15	cooling water tank
16	cooling water-temperature controller
17	high-pressure pump for atomizing cooling water
18	pipework for atomizing cooling water
20	cooling water
51	collision pressure sensor

Claims

1. A method for manufacturing atomized metal powder in which atomized metal powder having an amorphous material fraction of 90% or more is obtained, the method comprising ejecting high-pressure water so as to collide with a molten metal stream flowing vertically downward, separating the molten metal stream into metal powder, and cooling the metal powder,
wherein the high-pressure water collides with the molten metal with a collision pressure of 20 MPa or higher, and
wherein a temperature of the molten metal and/or a temperature of the high-pressure water are controlled so that the high-pressure water is in a subcritical state or a supercritical state on a collision surface with the molten metal.

2. The method for manufacturing atomized metal powder according to Claim 1, wherein an average temperature of the molten metal and the high-pressure water is 374°C or higher at a time of collision between the high-pressure water and the molten metal.

3. The method for manufacturing atomized metal powder according to Claim 1 or 2, wherein, when a flow rate of the molten metal stream per unit time is defined as Qm (kg/min) and an ejection rate of the high-pressure water per unit time is defined as Qaq (kg/min), a mass ratio (Qaq/Qm) is 35 or more.

4. The method for manufacturing atomized metal powder according to any one of Claims 1 to 3, wherein the atomized metal powder contains iron-group constituents (Fe, Ni, and Co) in a total amount of 76.0 at% or more in terms of atomic fraction and Cu in an amount of 0.1 at% or more and 2.0 at% or less in terms of atomic fraction.

5. The method for manufacturing atomized metal powder according to any one of Claims 1 to 3, wherein the atomized metal powder contains iron-group constituents (Fe, Ni, and Co) in a total amount of more than 82.5 at% and less than 86.0 at% in terms of atomic fraction, at least two selected from Si, P, and B, and Cu and has an average particle size of 5 µm or more.

6. The method for manufacturing atomized metal powder according to any one of Claims 1 to 5,
wherein the subcritical state is represented by a pressure of 0.5 MPa to 22 MPa and a water temperature of 150°C to 274°C, and
wherein the supercritical state is represented by a pressure of 22 MPa or higher and a water temperature of 374°C or higher.

FIG. 1

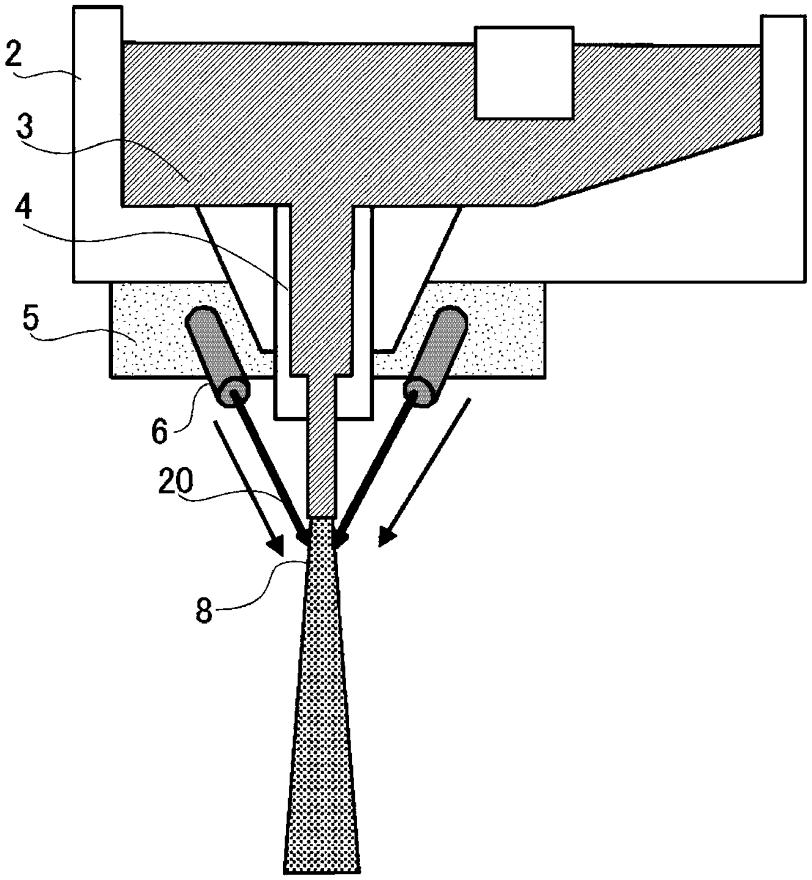


FIG. 2

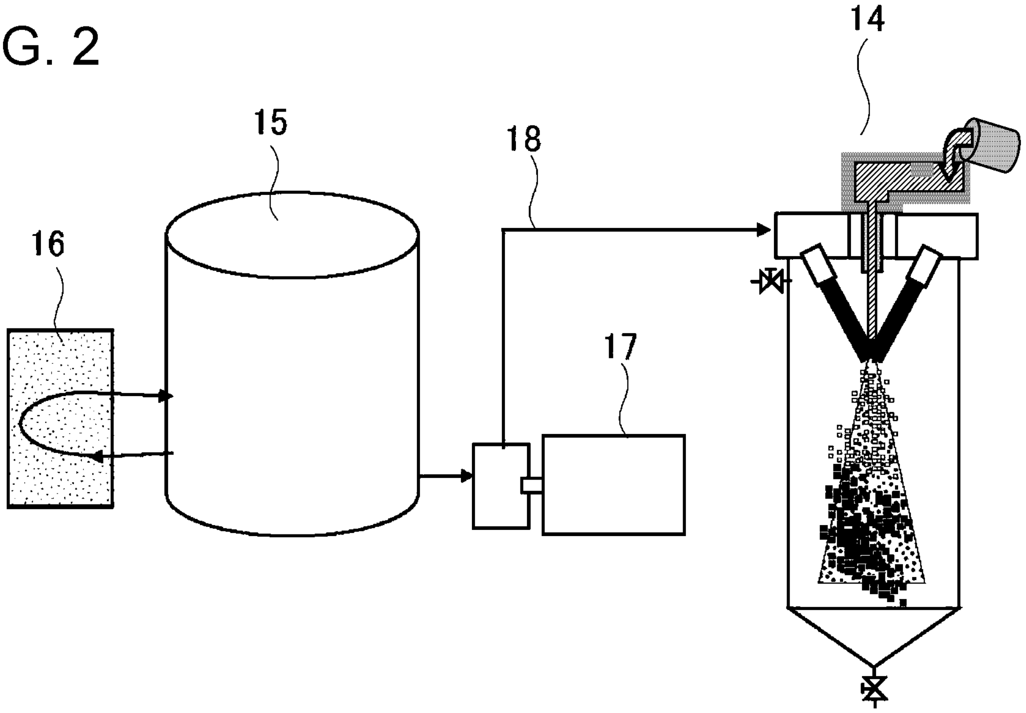


FIG. 3

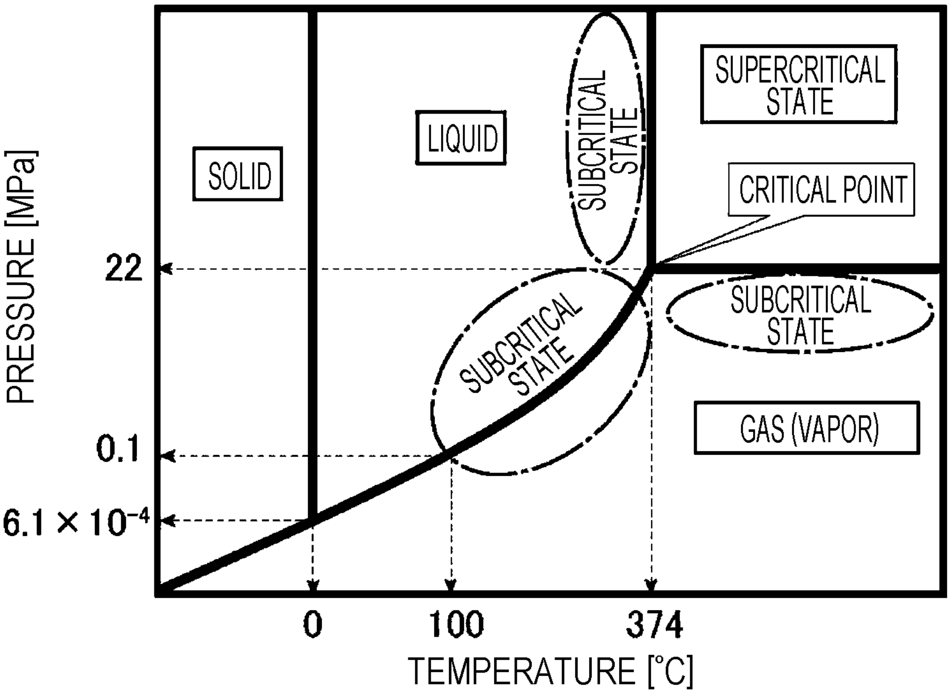

SOLID
LIQUID
SUBCRITICAL STATE
SUPERCRITICAL STATE
CRITICAL POINT
SUBCRITICAL STATE
SUBCRITICAL STATE
GAS (VAPOR)
PRESSURE [MPa]
22
0.1
6.1 × 10⁻⁴
0
100
374
TEMPERATURE [°C]

FIG. 4

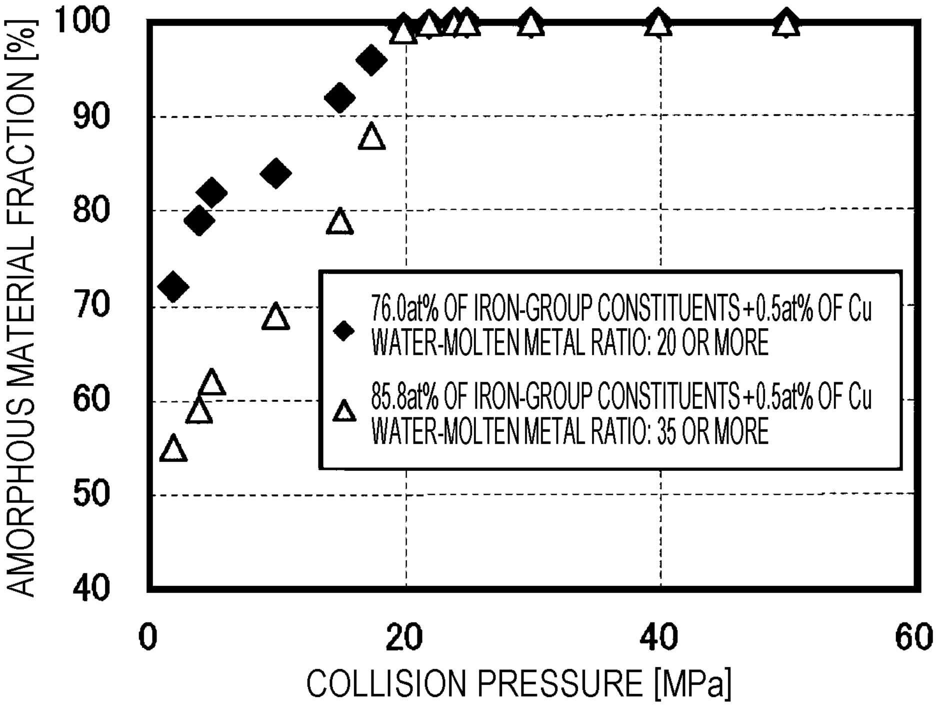

AMORPHOUS MATERIAL FRACTION [%]
100
90
80
70
60
50
40
0
20
40
60
COLLISION PRESSURE [MPa]
◆ 76.0at% OF IRON-GROUP CONSTITUENTS+0.5at% OF Cu WATER-MOLTEN METAL RATIO: 20 OR MORE
△ 85.8at% OF IRON-GROUP CONSTITUENTS+0.5at% OF Cu WATER-MOLTEN METAL RATIO: 35 OR MORE

FIG. 5

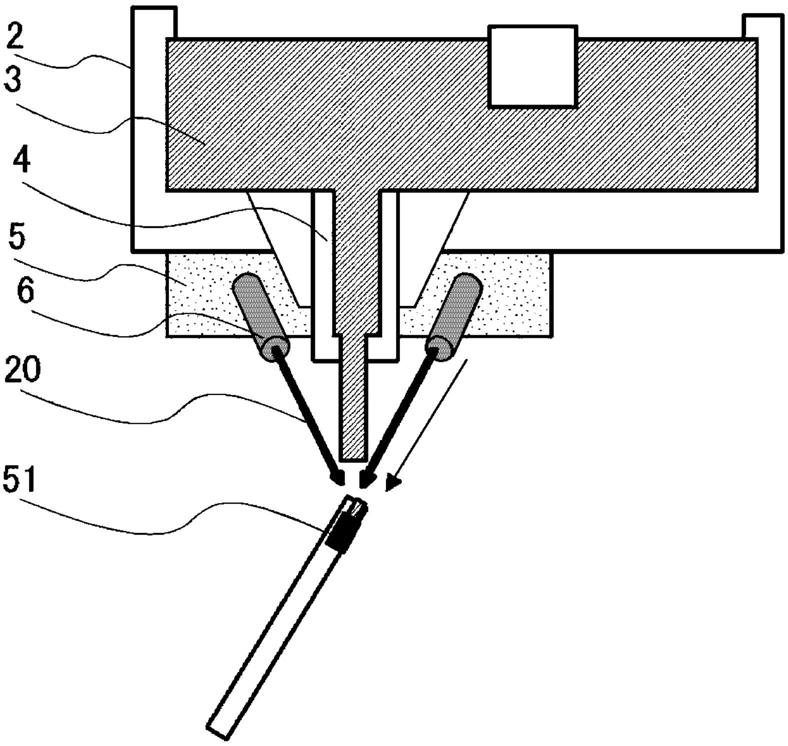
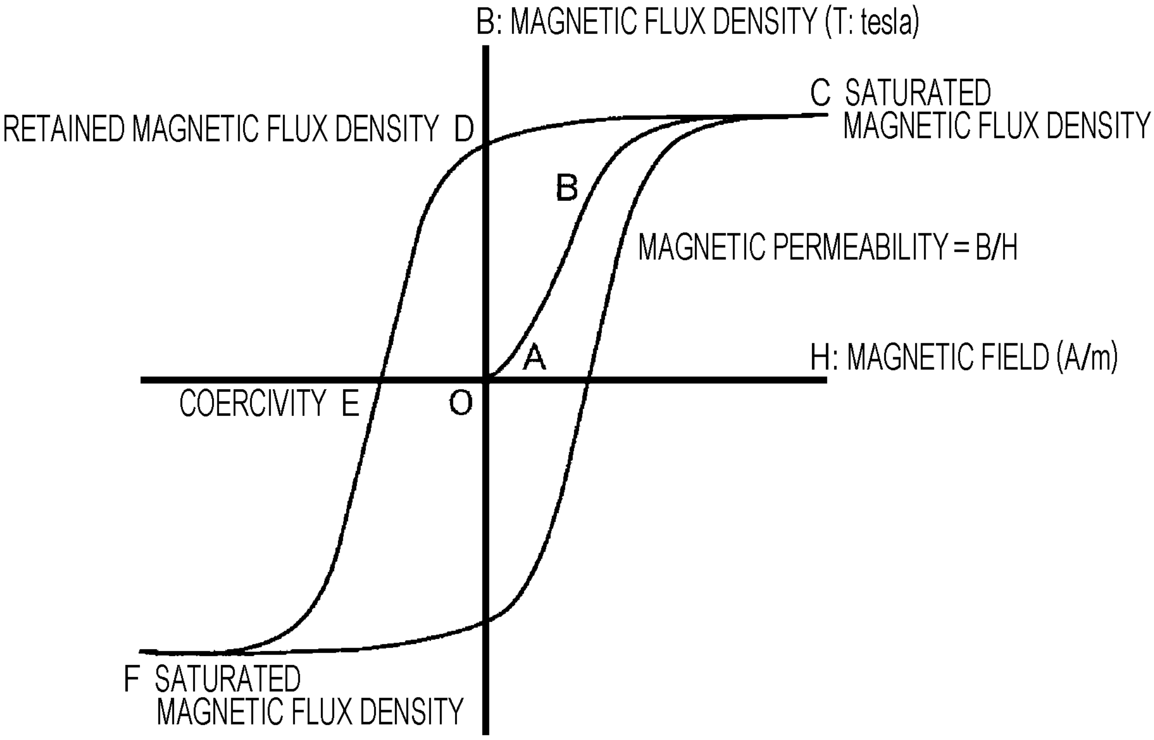

2
3
4
5
6
20
51

FIG. 6


B: MAGNETIC FLUX DENSITY (T: tesla)
C SATURATED MAGNETIC FLUX DENSITY
RETAINED MAGNETIC FLUX DENSITY D
B
MAGNETIC PERMEABILITY = B/H
A
H: MAGNETIC FIELD (A/m)
COERCIVITY E
O
F SATURATED MAGNETIC FLUX DENSITY

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2018/044727

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl. B22F9/08(2006.01)i, C22C38/00(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)
Int.Cl. B22F9/08, C22C38/00

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

Published examined utility model applications of Japan	1922-1996
Published unexamined utility model applications of Japan	1971-2019
Registered utility model specifications of Japan	1996-2019
Published registered utility model applications of Japan	1994-2019

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2016/157762 A1 (JFE STEEL CORPORATION) 06 October 2016, entire text & US 2018/0071826 A1 entire text & CN 107427926 A	1-6
A	JP 2002-004015 A (INOUE, Akihisa) 09 January 2002, entire text (Family: none)	1-6
A	JP 64-55308 A (HITACHI METALS, LTD.) 02 March 1989, entire text (Family: none)	1-6

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

* Special categories of cited documents:
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"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

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"&" document member of the same patent family

Date of the actual completion of the international search 11 January 2019 (11.01.2019)	Date of mailing of the international search report 29 January 2019 (29.01.2019)
Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer Telephone No.

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

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- **HIDEO TORAYA.** *Journal of the Crystallographic Society of Japan,* 1988, vol. 30 (4), 253-258 **[0031]**
- *National Research and Development Agencies,* 16 November 2017, https://www.jst.go.jp/pr/report/report27/grf2.html **[0055]**