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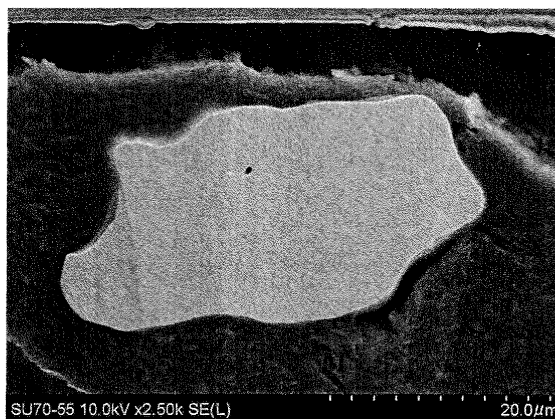
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(54) **POWDER AND METHOD FOR PRODUCING THE SAME**

(57) The powder of the invention comprises metal powder, an apatite layer covering the metal powder and silica particles attached to the metal powder or apatite layer. The powder of the invention allows annealing to

be carried out at high temperature without destruction of the insulating layer during production of powder magnetic cores. The insulating property of the insulating layer is therefore maintained, and a powder magnetic core with sufficiently high magnetic permeability can be obtained.

Fig.1



Description**Technical Field**

5 **[0001]** The present invention relates to a powder suitable as a starting powder for production of a low iron loss powder magnetic core.

Background Art

10 **[0002]** A large variety of familiar products exist that utilize electromagnetism, including transformers, electric motors, generators, speakers, induction heaters, actuators and the like. For higher performance and size reduction, it is essential to improve the performance of the magnetic core, which is a green compact of a soft magnetic material.

15 **[0003]** Conventionally, the magnetic core is produced by alternately layering a plurality of silicon steel thin-films and insulating layers, and punching the stack with a die (magnetic steel sheet). However, this method is often inconvenient for product downsizing and unsuitable for forming complex shapes, while reduced eddy current loss has also been a problem.

20 **[0004]** These problems have been examined with recent research and development focused on powder magnetic cores obtained by compression molding soft magnetic metal powder, as magnetic cores with high moldability and low production cost.

25 **[0005]** Such powder magnetic cores are required to increase magnetic permeability to increase the flux density. Magnetic cores for motors, in particular, are usually used in an alternating field, and since high iron loss impairs the energy conversion efficiency they are required to have low iron loss.

30 **[0006]** Iron loss includes hysteresis loss, eddy current loss and residual loss, with hysteresis loss and eddy current loss mainly constituting the problems.

35 **[0007]** Increased hysteresis loss in a powder magnetic core is due to application of a large degree of working strain to the soft magnetic metal powder when the soft magnetic metal powder is compression molded into a powder magnetic core. In order to reduce hysteresis loss, therefore, it is effective to anneal the obtained compact after compression molding to relieve the strain on the soft magnetic metal powder, for which an annealing temperature of 600°C or higher is considered preferable.

40 **[0008]** On the other hand, covering the soft magnetic metal powder with an insulating material is effective for reducing eddy current loss. Insulating materials commonly used in the prior art, however, decompose when annealed to reduce hysteresis loss, because of the low heat resistance of the insulating material, and the insulating property is markedly impaired as a result. It has therefore been a primary goal to achieve both reduced eddy current loss and reduced hysteresis loss.

45 **[0009]** Insulating materials with excellent heat resistance are being developed toward reaching this goal. In particular, the use of iron powder as soft magnetic metal powder is a target of much research and development, as it allows production of powder magnetic cores with low cost and high flux density. Patent document 1, for example, proposes a method of employing silica particles as an insulating film with excellent heat resistance. The document discloses a method in which iron powder with a phosphated surface is mixed with a silica particle-containing suspension, and the mixture is dried to obtain metal powder coated with silica powder.

50 **[0010]** However, when it is attempted to produce a powder magnetic core using such iron powder coated with silica particles, it has been necessary to use a higher annealing temperature than the ordinary temperature of around 600°C (for example, 800°C or higher) to obtain sufficient bonding force between the metal powder. An excessively high annealing temperature can lower the magnetic properties of the powder magnetic core because the Curie temperature of iron is 769°C.

55 **[0011]** Patent document 2 proposes a method in which an oxide layer and an insulating layer are formed on the surface of soft magnetic metal powder and subjected to bond-strengthening treatment in a reducing atmosphere under high-temperature conditions, to form a monolayer with an excellent insulating property on the surface of the soft magnetic metal powder.

[Patent document 1] Japanese Unexamined Patent Publication HEI No. 9-180924

[Patent document 2] Japanese Unexamined Patent Publication No. 2007-194273

Disclosure of the Invention

60 **Problems to be Solved by the Invention**

[0012] Soft magnetic metal powder produced by the method disclosed in Patent document 2 can be used to provide a powder magnetic core with excellent heat resistance. However, because of the high energy cost associated with

annealing in this method and the fact that the method is not suitable for mass production, more simple methods for obtaining coated soft magnetic metal powder with excellent heat resistance have been considered.

[0013] Yet, although flux density can be effectively increased by forming a very thin and broad insulating layer on soft magnetic metal powder, no simple and low-cost method for doing this has been known.

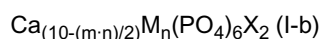
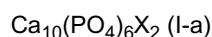
[0014] The present invention has been accomplished in light of the problems of the prior art as described above, and its object is to provide a soft magnetic metal starting powder that can both reduce hysteresis loss and reduce eddy current loss in powder magnetic cores, while also having low iron loss and high flux density.

Means for Solving the Problems

[0015] In order to solve the problems described above, the invention provides a powder comprising metal powder, an apatite layer covering the metal powder and silica particles attached to the metal powder or apatite layer.

[0016] According to the invention, metal powder is covered with an apatite layer and silica particles are attached to the metal powder or apatite layer, to allow forming an insulating film on the metal powder surface that can withstand annealing temperatures of 600°C or higher. The use of this construction and its effect is based on knowledge of the present inventors that formation of a satisfactory heat-resistant insulating film that can withstand annealing temperatures of 600°C or higher is effective for reducing hysteresis loss.

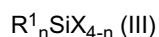
[0017] According to the invention, the apatite layer preferably contains a compound represented by the following formula (I-a) or (I-b).



(In the formulas, M represents a cation-donating atom or group of atoms, m represents the valency of the cation donated by M, n is greater than 0 and not greater than 5, and X represents an atom or group of atoms that donates a monovalent anion.)

[0018] The silica particles are preferably silica particles that have been surface-modified with an organic group.

[0019] The silica particles that have been surface-modified with an organic group are preferably silica particles that have been surface-modified using a compound represented by the following formula (II) or (III).



(In the formulas, n is an integer of 1-3, R¹ and R² represent monovalent organic groups, and X represents a halogen.)

[0020] The metal powder is preferably a soft magnetic material powder.

[0021] The powder of the invention is suitable as a powder for a powder magnetic core.

[0022] The invention provides a method for producing powder which comprises a first step of covering metal powder with apatite, a second step of attaching silica powder to the metal powder surface or apatite surface obtained in the first step, and a third step of pre-curing the powder obtained in the second step at not greater than 350°C to obtain powder comprising the metal powder, the apatite layer covering the metal powder, and silica particles attached to the metal powder or apatite layer.

[0023] The metal powder provided in the first step is preferably phosphated metal powder.

Effect of the Invention

[0024] The powder of the invention is covered with an insulating layer comprising an apatite layer and silica particles attached thereto, and the insulating layer has excellent insulating properties and heat resistance. Annealing can therefore be carried out at high temperature without destruction of the insulating layer during production of powder magnetic cores. The insulating property of the insulating layer is thus maintained, and a powder magnetic core with sufficiently high magnetic permeability can be obtained.

Brief Description of the Drawings

[0025] Fig. 1 is a photograph showing a scanning electron microscope (SEM) image of a cross-section of the hydroxyapatite-covered iron powder obtained in Example 1 (magnification: 2500x).

Fig. 2 is a photograph showing an SEM image of a cross-section of the hydroxyapatite-covered iron powder obtained in Example 1 (magnification: 50000x).

Fig. 3 is a photograph showing an SEM image of a cross-section of the nanosilica-attached hydroxyapatite-covered iron powder obtained in Example 1 (magnification: 1000x).

Fig. 4 is a photograph showing an SEM image of a cross-section of the nanosilica-attached hydroxyapatite-covered iron powder obtained in Example 1 (magnification: 100000x).

Best Mode for Carrying Out the Invention

[0026] One mode of the powder of the invention is a powder comprising metal powder, an apatite layer covering the metal powder and silica particles attached to the metal powder or apatite layer. Each of the constituent elements of the powder of the invention will now be explained.

(Metal powder)

[0027] The metal powder used for the invention is not particularly restricted so long as it is metal powder with ferromagnetism and exhibiting high saturated flux density, and as specific examples there may be mentioned soft magnetic materials such as iron powder, silicon-steel powder, sendust powder, amorphous powder, permendur powder, soft ferrite powder, amorphous magnetic alloy powder, nanocrystal magnetic alloy powder and permalloy powder, which may be used alone or in mixtures of two or more. Iron powder is preferred among these from the viewpoint of strong magnetism and low cost.

[0028] Among iron powders, pure iron powder is especially preferred from the standpoint of excellent magnetic properties including saturated flux density and magnetic permeability, and excellent compressibility. As specific examples of such pure iron powders there may be mentioned atomized iron powder, reduced iron powder and electrolytic iron powder, such as 300NH by Kobe Steel, Ltd.

[0029] The metal powder used may be the metal powder with a modified element composition in a range that does not adversely affect the compressibility or the magnetic properties of the powder magnetic core. Specifically, elemental phosphorus may be added to prevent oxidation of the metal powder, or an element such as cobalt, nickel, manganese, chromium, molybdenum or copper may be added to improve the magnetic properties.

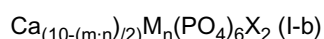
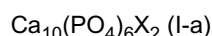
[0030] There are no particular restrictions on the particle size of the metal powder, and it may be appropriately selected according to the purpose and properties required for the powder magnetic core. Generally speaking, it may be selected so that the size of the particles as observed under a scanning electron microscope (SEM) is in the range of 1 μm -300 μm . A particle size of 1 μm or greater will tend to facilitate molding during production of the powder magnetic core, while a particle size of 300 μm or smaller will help prevent increased eddy current of the powder magnetic core and tend to facilitate coating of the apatite layer. The mean particle size (the mean secondary particle size determined by screening) is preferably 50-250 μm .

[0031] The form of the metal powder is not particularly restricted and may be spherical or globular, or flat powder obtained by flattening treatment by a known process or machining method.

(Apatite layer)

[0032] The apatite layer covering the surface of the powder of the invention functions as an insulating film for the metal powder. From this viewpoint, the apatite layer preferably has a coating film structure covering the surface of the metal powder in a laminar fashion.

[0033] An apatite layer is a layer composed of a substance with an apatite structure. As specific preferred examples of substances with apatite structures for the apatite layer there may be mentioned compounds represented by the following formula (I-a) or (I-b).



(In the formulas, M represents a cation-donating atom, m represents the valency of the cation donated by M, n is greater than 0 and not greater than 5, and X represents an atom or group of atoms that donates a monovalent anion.)

[0034] In formula (I-b), the cation-donating atom M is preferably a metal that can replace calcium. As such metals there may be mentioned, specifically, metals with ion radii of 0.80-1.40 Å, such as sodium, magnesium, potassium, calcium, scandium, titanium, chromium, manganese, iron, cobalt, nickel, zinc, strontium, yttrium, zirconium, ruthenium, rhodium, palladium, silver, cadmium, indium, tin, antimony, tellurium, barium, lanthanum, cerium, praseodymium, neo-

dymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, hafnium, platinum, gold, mercury, thallium, lead or bismuth. M in formula (I-b) may be of a single type or two or more types. The range for n in formula (I-b) is greater than 0 and not greater than 5, more preferably greater than 0 and not greater than 2.5, and even more preferably greater than 0 and not greater than 1.0. Also, each X in formula (I-a) and (I-b) is preferably hydroxyl (OH) or a halogen (such as F, Cl, Br or I) and is more preferably hydroxyl or fluorine. X is preferably a hydroxyl group from the viewpoint of excellent coatability onto metal powder, and it is preferably fluorine from the viewpoint of excellent strength.

[0035] The substance with an apatite structure for the apatite layer is more preferably a compound represented by formula (I-a), and especially preferably hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) or fluoroapatite ($\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2$), from the viewpoint of excellent insulating properties, heat resistance and dynamic properties when made into a powder magnetic core.

[0036] The term "covering the metal powder with the apatite layer" in regard to the powder of the invention means that at least a portion of the metal powder is covered by the apatite layer. The term "apatite-covered metal powder" used below, therefore, includes not only metal powder completely covered with apatite but metal powder that is partially exposed. The extent of coverage of the metal powder by the apatite layer is preferably to a higher coverage factor from the viewpoint of facilitating adhesion of silica, described hereunder, and resulting in improved transverse strength. Specifically, preferably at least 90% of the surface, more preferably at least 95% and even more preferably all (essentially 100%) of the metal powder is covered by the apatite layer.

[0037] The apatite layer in the powder of the invention has a thickness of preferably 10 nm-1000 nm and more preferably 20-500 nm. A thickness of 10 nm or greater will tend to provide an insulating effect, while a thickness of not greater than 1000 nm will tend to provide a density-improving effect.

[0038] The method of forming the apatite layer on the metal powder may be a method in which an aqueous solution containing calcium ion or additionally the ion of the cation-donating atom or group of atoms M of formula (1-b) in a prescribed ratio is reacted with an aqueous solution containing phosphate ion, to deposit a substance that adopts an apatite structure on the metal powder surface. In order to obtain a layer with an apatite structure, it is essential to control the reaction mixture to between the neutral and basic range (pH = 6.0 or higher). In the acidic range, a calcium phosphate layer may sometimes be deposited in addition to the substance with an apatite structure.

[0039] When hydroxyapatite is deposited as the apatite layer, a method using a calcium nitrate aqueous solution and ammonium dihydrogenphosphate aqueous solution may be employed. The stoichiometric composition of the hydroxyapatite obtained in this manner is $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, but it may be a nonstoichiometric composition so long as the majority is an apatite structure and it can be maintained, and for example, a portion may be $\text{Ca}_{10-Z}(\text{HPO}_4)_Z(\text{PO}_4)_{6-Z}(\text{OH})_{2-Z}$ ($0 < Z \leq 1$, $1.50 \leq \text{Ca/P (atomic weight ratio)} < 1.67$).

[0040] The amount of apatite layer starting material added is preferably 0.1-1.0 part by mass, more preferably 0.4-0.8 part by mass and even more preferably 0.5-0.7 part by mass with respect to 100 parts by mass of the metal powder. An amount of at least 0.1 part by mass will tend to result in adequate resistivity when the powder is formed into a powder magnetic core. A uniform insulating layer can also be formed on the powder, and an effect of improved insulation can be satisfactorily obtained. An amount of not greater than 1.0 part by mass will help prevent reduction in the compact density when the powder is formed into a powder magnetic core. The mass of apatite layer can be determined by quantifying the amount of calcium (and metal M) by elemental analysis of the obtained powder.

(silica particles)

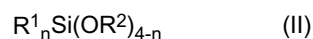
[0041] The silica particles used for the powder of the invention may be any that are known in the prior art, among which fumed silica and colloidal silica may be mentioned specifically, but colloidal silica is preferred from the viewpoint of easy manageability. There are no restrictions on the shapes of the silica particles.

[0042] The particle size of the silica particles may be any of various sizes, but silica particles having a submicron particle size are preferred for film formability. Specifically, the mean primary particle size of the silica particles is preferably not greater than 50 nm, more preferably not greater than 30 nm and even more preferably not greater than 20 nm.

[0043] The silica particles are preferably dispersed without aggregation in an organic solvent. For improved dispersibility of the silica particles, the silica particle surfaces may be modified with an organic group. As examples of organic groups there may be mentioned cyclohexyl, phenyl, benzyl, phenethyl and C1-C6 (1-6 carbon atoms) alkyl groups.

[0044] The method of modifying the silica particle surfaces with the organic group may be a method of reacting the silica particle surfaces with a silane compound having an organic group in the molecular structure. This can increase the transverse strength and often improve the resistivity, when the powder is formed into a powder magnetic core.

[0045] Specific silane compounds include alkoxysilanes represented by the following formula (II) and halogenosilane compounds represented by the following formula (III).





(In the formulas, n is an integer of 1-3, R¹ and R² represent monovalent organic groups, and X represents a halogen.)
 [0046] R¹ in formulas (II) and (III) is the organic group that is to modify the silica particles, and specifically there may be mentioned cyclohexyl, phenyl, benzyl, phenethyl and C1-C6 (1-6 carbon atoms) alkyl groups. R² may be a monovalent organic group, and specifically methyl, ethyl or the like. X may be chloro, bromo, iodo or the like.

[0047] Specific examples of alkoxysilanes represented by formula (II) include trimethoxysilanes such as methyltrimethoxysilane, ethyltrimethoxysilane, n-propyltrimethoxysilane, iso-propyltrimethoxysilane, n-butyltrimethoxysilane, tert-butyltrimethoxysilane, n-pentyltrimethoxysilane, n-hexyltrimethoxysilane, cyclohexyltrimethoxysilane, phenyltrimethoxysilane, benzyltrimethoxysilane and phenethyltrimethoxysilane;

triethoxysilanes such as methyltriethoxysilane, ethyltriethoxysilane, n-propyltriethoxysilane, iso-propyltriethoxysilane, n-butyltriethoxysilane, tert-butyltriethoxysilane, n-pentyltriethoxysilane, n-hexyltriethoxysilane, cyclohexyltriethoxysilane, phenyltriethoxysilane, benzyltriethoxysilane and phenethyltriethoxysilane;

dimethoxysilanes such as dimethyldimethoxysilane, ethylmethyldimethoxysilane, methyl-n-propyldimethoxysilane, methyl-iso-propyldimethoxysilane, n-butylmethyldimethoxysilane, methyl-tert-butyldimethoxysilane, methyl-n-pentyldimethoxysilane, n-hexylmethyldimethoxysilane, cyclohexylmethyldimethoxysilane, methylphenyldimethoxysilane, benzylmethyldimethoxysilane and phenethylmethyldimethoxysilane;

and diethoxysilanes such as dimethyldiethoxysilane, ethylmethyldiethoxysilane, methyl-n-propyldiethoxysilane, methyl-iso-propyldiethoxysilane, n-butylmethyldiethoxysilane, methyl-tert-butyldiethoxysilane, methyl-n-pentyldiethoxysilane, n-hexylmethyldiethoxysilane, cyclohexylmethyldiethoxysilane, methylphenyldiethoxysilane, benzylmethyldiethoxysilane and phenethylmethyldiethoxysilane.

[0048] Specific examples of halogenosilane compounds represented by formula (III) include:

trichlorosilanes such as methyltrichlorosilane, ethyltrichlorosilane, n-propyltrichlorosilane, iso-propyltrichlorosilane, n-butyltrichlorosilane, tert-butyltrichlorosilane, n-pentyltrichlorosilane, n-hexyltrichlorosilane, cyclohexyltrichlorosilane, phenyltrichlorosilane, benzyltrichlorosilane and phenethyltrichlorosilane;

and dichlorosilanes such as dimethyldichlorosilane, ethylmethyldichlorosilane, methyl-n-propyldichlorosilane, methyl-iso-propyldichlorosilane, n-butylmethyldichlorosilane, methyl-tert-butyldichlorosilane, methyl-n-pentyldichlorosilane, n-hexylmethyldichlorosilane, cyclohexylmethyldichlorosilane, methylphenyldichlorosilane, benzylmethyldichlorosilane and phenethylmethyldichlorosilane.

[0049] These silane compounds may be used alone or in combinations of two or more.

[0050] The surface modification of the silica particles can generally be accomplished by adding the alkoxysilane compound or halogenosilane compound to a dispersion of the silica particles and stirring the mixture. In this case, it is preferably added in a range of 0.4-0.6 part by weight to 1 part by solid weight of the silica particles. Limited to not greater than 0.6 part by weight, there will be no residual unreacted silane compound added, and in an amount of at least 0.4 part by weight a sufficient effect of organic group modification of the silica particles can be achieved. The silica particles may be dispersed in water or dispersed in an organic solvent.

[0051] To promote rapid modification reaction of the organic group onto the silica particle surfaces under mild conditions, it is preferred to use an acid catalyst such as an inorganic acid, organic acid or acidic ion exchange resin. In this case it is particularly preferred to use hydrochloric acid, nitric acid, acetic acid, citric acid, formic acid, oxalic acid or the like. Common acids can react with apatite and impair its properties, and therefore hydrochloric acid and acetic acid are especially preferred for their high volatility to escape from the system. The amount of acid catalyst added is preferably 0.05-0.1 part by weight to 1 part by solid weight of the silica particles.

[0052] The temperature for the modification reaction is preferably 0-50°C and more preferably 10-40°C, to prevent aggregation of the silica particles. Also, the silica particles are preferably dispersed in an organic solvent such as isopropyl alcohol, polyethyleneglycol monomethyl ether acetate, toluene or xylene.

(Production method)

[0053] The method for producing the powder of the invention comprises a first step of covering metal powder with apatite to form metal powder covered with an apatite layer (hereunder referred to as "apatite-covered metal powder"), a second step of attaching silica powder to the metal powder or apatite layer of the apatite-covered metal powder obtained in the first step, and a third step of pre-curing the powder obtained in the second step at not greater than 350°C to obtain powder comprising the metal powder, the apatite layer covering the metal powder, and silica particles attached to the metal powder or apatite layer.

(Phosphating treatment of metal powder)

[0054] The metal powder provided in the first step is preferably phosphated metal powder, from the viewpoint of preventing oxidation of the metal powder. In the method for producing powder according to the invention, the phosphating treatment may be carried out before the first step, or a commercially available metal powder that has been subjected to phosphating treatment may be used. The phosphating treatment may be carried out by a method known in the prior art.

(Formation of apatite layer)

[0055] The method of forming the apatite layer on the metal powder may be a method in which an aqueous solution containing calcium ion (if necessary with the ion of a cation-donating atom or group of atoms M other than calcium) is reacted with an aqueous solution containing phosphate ion, as explained above, to deposit apatite on the metal powder surface. Specifically, the aqueous solution used as the calcium source may be placed in a flask together with the metal powder and stirred therewith while adding the aqueous solution as the phosphate source in a dropwise manner. Alternatively, water and the metal powder may be placed in a flask and stirred while adding the aqueous solution as the calcium source and the aqueous solution as the phosphate source in a dropwise manner, either simultaneously or successively. In the case of successive dropwise addition, they may be added in either order.

[0056] The calcium source is not particularly restricted so long as it is a water-soluble calcium compound, and as specific examples there may be mentioned calcium salts of inorganic bases such as calcium hydroxide, calcium salts of inorganic acids such as calcium nitrate, calcium salts of organic acids such as calcium acetate, and calcium salts of organic bases. As phosphate sources there may be mentioned phosphoric acid, and phosphoric acid salts such as ammonium dihydrogenphosphate and diammonium hydrogenphosphate.

[0057] In order to obtain a layer with an apatite structure, the reaction mixture is preferably in the neutral range to basic range, with a pH of preferably 7 or higher, more preferably 8 or higher, even more preferably 9 or higher and especially preferably 10 or higher. Because a layer of calcium phosphate other than apatite may be deposited in the acidic range, the aqueous solution as the calcium source and the aqueous solution as the phosphate source is preferably preadjusted to a pH of 7 or higher with a base such as ammonia water.

[0058] The reaction temperature may be room temperature, but it is preferably 50°C or higher, more preferably 70°C or higher and even more preferably 90°C or higher to promote the reaction. If the solvent is water, the upper limit for the temperature will be the reflux temperature of the reaction mixture, i.e. near 100°C.

[0059] The reaction time will depend on the concentrations of the aqueous solution as the calcium source and the aqueous solution as the phosphate source, with a shorter reaction time being sufficient for higher concentrations and a longer reaction time preferred for lower concentrations. The concentrations of the aqueous solution as the calcium source and the aqueous solution as the phosphate source in the production method of the invention are preferably each in the range of 0.003-0.5M, in which case the reaction time is preferably 1-10 hours.

(Attachment of silica powder)

[0060] Silica particles are attached to the apatite-covered metal powder obtained in the manner described above. The method may involve adding a dispersion of the silica particles to the apatite-covered metal powder and shaking and stirring the mixture. If a commercially available organosilica sol is used, it may be diluted to an appropriate concentration. When the surfaces of the silica particles are surface-modified with an organic group such as a silane compound in a commercially available organosilica sol as described above, the reaction mixture used for the surface modification may be used directly. The silica particles used in this case may be attached to an apatite layer or they may be attached to the exposed metal powder surface at defect sections where the apatite layer covering is lacking.

[0061] The solvent used to disperse the silica particles is not particularly restricted, and as specific examples there may be mentioned alcohol-based solvents such as isopropyl alcohol, ketone-based solvents such as methyl ethyl ketone, and aromatic-based solvents such as toluene. Particularly preferred are aromatic solvents that allow the colloidal solution state of the silica particles in the organosilica sol to be maintained more easily.

(Pre-curing)

[0062] The apatite-covered metal powder having silica particles attached to the surface is then pre-cured at not greater than 350°C. This can cure the apatite layer to form a strong heat-resistant coating. Without pre-curing, the silica particles on the surface will become embedded in the apatite layer when the starting powder is compression molded to produce a powder magnetic core, tending to result in an insufficient insulating property. The temperature for pre-curing is preferably 100-300°C.

[0063] The amount of silica particles used for the invention is preferably 0.05-1.0 part by mass with respect to 100

parts by mass of the metal powder used. An amount of at least 0.05 part by mass will allow uniform coverage of the metal powder by the silica particles, tending to produce an effect of improving the insulating property. An amount of not greater than 1.0 part by mass will help prevent reduction in the compact density when the powder is formed into a powder magnetic core, as well as prevent reduction in the transverse strength of the obtained powder magnetic core.

(Production of powder magnetic core)

[0064] The powder for a powder magnetic core according to the invention may be formed into a powder magnetic core by compression molding a mixed powder with admixture of a lubricant if necessary. The lubricant may also be used by coating and drying a dispersion thereof onto the die wall face. As lubricants there may be used metal soaps such as zinc stearate, calcium stearate and lithium stearate, long-chain hydrocarbons such as waxes, and silicone oils. The molding pressure is preferably 500-1500 MPa. The obtained powder magnetic core may be annealed to lower the hysteresis loss. The annealing temperature in this case is preferably selected within the range of 500-800°C. The annealing is preferably carried out in an inert gas such as nitrogen or argon.

[0065] The powder magnetic core produced by this method exhibits high compact density and insulating properties. The mechanism by which these properties are exhibited has not been fully elucidated, but the present inventors conjecture that it is the following. Specifically, when the apatite layer covers the metal powder, the high adsorptive power of the apatite facilitates attachment of the silica particles to the metal powder. It is believed that the attached silica particles effectively fill the fissures in the apatite layer created during molding, thereby allowing a high compact density (for example, 7.0 g/cm³ or greater) and high heat resistance and insulation to be maintained. The reason that a particle size below the submicron level is preferred for the silica particles may be that smaller silica particles move more easily and the silica particles therefore more effectively fill in the fissures of the apatite layer.

[0066] The compact density of the powder magnetic core formed from the powder of the invention is preferably 7.0 g/cm³ or greater and more preferably 7.4 g/cm³ or greater. A density of at least 7.4 g/cm³ will tend to improve the flux density of the powder magnetic core.

[0067] The electrical resistance value of the surface of the powder magnetic core is preferably at least 30 μΩm, more preferably at least 50 μΩm and even more preferably at least 90 μΩm. An electrical resistance of at least 30 μΩm will tend to produce an effect of reducing the eddy current loss of the powder magnetic core.

Examples

[0068] The present invention will now be explained in greater detail through the following examples, with the understanding that these examples are in no way limitative on the invention.

[Example 1]

[0069] In a 300 mL 4-necked flask there were placed 75 mL (1.79 mmol, 0.024 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water, and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.). Also, 75 mL (1.07 mmol, 0.014 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred at room temperature (25°C) while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes.

[0070] Next, the 4-necked flask was reacted for 2 hours while stirring in an oil bath at 90°C. The obtained slurry was suction filtered and the filtered product was dried in an oven at 110°C to obtain a gray powder (yield: 96 mass%). Upon analyzing the atomic abundance ratio near the surface of the obtained powder by X-ray photoelectron spectroscopy (XPS), the atomic abundance ratio was Fe: 4.58%, Ca: 15.7% and the Ca/P ratio (molar ratio) was 1.64, and the iron powder was confirmed to be covered with hydroxyapatite.

[0071] Next, 20 g of the obtained apatite-covered iron powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were mixed and shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and the contents were removed into a stainless steel dish and pre-cured at 200°C for 30 minutes. The pre-cured powder was passed through a 250 μm sieve to remove the giant aggregate particles, to obtain nanosilica-attached apatite-covered iron powder.

[0072] Figs. 1 and 2 show SEM photographs of the cross-sections of apatite-covered iron powder obtained in this manner, and Figs. 3 and 4 show SEM photographs of the cross-sections of nanosilica-attached apatite-covered iron powder. It was confirmed that a hydroxyapatite layer and nanosilica layer had been formed on the particle surfaces.

[0073] After packing 5.92 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa. The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity

(resistivity) was measured with a four-terminal resistivity meter to be 296 $\mu\Omega\text{m}$. The density was 7.48 g/cm^3 . The tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 91 $\mu\Omega\text{m}$. The density was 7.47 g/cm^3 .

[Comparative Example 1]

[0074] Hydroxyapatite-covered iron powder was prepared as follows, partly in the same manner as Example 1. Specifically, in a 300 mL 4-necked flask there were placed 75 mL (1.79 mmol, 0.024 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water, and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.). Also, 75 mL (1.07 mmol, 0.014 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred at room temperature (25°C) while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes.

[0075] Next, the 4-necked flask was reacted for 2 hours while stirring in an oil bath at 90°C. The obtained slurry was then suction filtered and the filtered product dried in an oven at 110°C to obtain a gray powder. (Yield: 96 mass%). The obtained powder was passed through a 250 μm sieve to obtain apatite-covered metal powder. After packing 5.95 g of the obtained apatite-covered metal powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa. The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 144 $\mu\Omega\text{m}$. The density was 7.54 g/cm^3 . The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 0.54 $\mu\Omega\text{m}$. The density was 7.53 g/cm^3 .

[Comparative Example 2]

[0076] Nanosilica was attached to iron powder by the method of attaching nanosilica used in Example 1, but without providing an apatite layer. Specifically, 20 g of iron powder (pure iron powder 300NH by Kobe Steel, Ltd.) and 2 g of a nanosilica-toluene solution (solid concentration: 3.0 mass%) were mixed and shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and pre-cured at 200°C for 30 minutes. The pre-cured powder was passed through a 250 μm sieve to remove the giant aggregate particles, to obtain nanosilica-attached metal powder. A 5.99 g portion of the obtained powder was molded at 1000 MPa into a cylindrical tablet with a diameter of 1.4 cm and a thickness of 5.145 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 79 $\mu\Omega\text{m}$. The density was 7.57 g/cm^3 . The polished tablet was annealed and fired under a nitrogen atmosphere, at 600°C for one hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 20 $\mu\Omega\text{m}$. The density was 7.57 g/cm^3 .

[0077] The results of measuring the density and resistivity of the powder magnetic core obtained in this manner are shown in Table 1.

[0078]

[Table 1]

Compact	Hydroxy-apatite covering	Silica particle attachment	Density (g/cm^3) after 600°C annealing	Resistivity ($\mu\Omega\text{m}$)	Resistivity ($\mu\Omega\text{m}$) after 600°C annealing
Example 1	Occurred	Occurred	7.47	296	91
Comp. Ex. 1	Occurred	None	7.53	144	0.54
Comp. Ex. 2	None	Occurred	7.57	79	20

[0079] Judging from Table 1, hydroxyapatite covering and silica particle attachment are both essential for obtaining high resistivity. Also, the compact density in Example 1 did not lower than the compact densities in Comparative Example 1 and Comparative Example 2, even though the powder in Example 1 was subjected to hydroxyapatite covering and silica particle attachment. This is attributed to destruction during compression molding, and embedding of the silica particles in the pores at the fissures of the produced apatite layer.

[0080] Next, in order to estimate the adsorptive strength between the apatite layer and silica particles, silica particles were attached to pure iron powder having a different surface form, and apatite-covered iron powder, and the degree of silica particles remaining on the surface was compared by quantitative analysis. As the method, 3.0 g of each powder

was added to 5.0 g of organosilica sol solution (medium: toluene) containing silica particles with a mean particle size of 20 nm measured by dynamic light scattering using an HPPS by Malvern Co. (solid concentration: 3.0 mass%), that had been placed in a glass screw tube with a maximum volume of 10 mL. The screw tube was stirred for 3 hours with a mix rotor set to a rotational speed of 105 rpm. The stirred solution was suction filtered using No.5B (JIS P3801) filter paper for quantitative analysis, and the filtered product was rinsed with toluene and vacuum dried to obtain each powder. The obtained powder was subjected to elemental analysis by ICP-OES, and the silica particles attached to the powder were quantified based on the quantity of silicon atoms. The results are shown in Table 2.

[0081]

[Table 2]

No.	Powder	Si adsorption (ppm by mass)
1	Pure iron powder (300NH)	160
2	Apatite-covered iron powder	360

[0082] According to the results shown in Table 2, the quantity of silicon atoms quantified from the apatite-covered iron powder was approximately twice that of the pure iron powder. Since the silicon atoms derive only from the silica particles, this indicated an increased degree of silica particle attachment, and stronger adsorptive power of the silica particles with the apatite layer than with the pure iron powder surface layer.

[Example 2]

[0083] After adding the iron powder to the calcium nitrate aqueous solution as in Example 1, an additional step of stirring for 15 minutes in an oil bath at 30°C was carried out.

[0084] Specifically, in a 300 mL 4-necked flask there were placed 75 mL (1.79 mmol, 0.024 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (1.07 mmol, 0.014 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes.

[0085] The oil bath temperature was then raised from 30°C to 90°C over a period of 10 minutes, and reaction was conducted at 90°C for 2 hours while stirring. The obtained slurry was suction filtered and the filtered product was dried in an oven at 110°C to obtain a gray powder. Upon analyzing the atomic abundance ratio near the surface of the obtained powder by XPS, the atomic abundance ratio was Fe: 3.31%, Ca: 17.1% and the Ca/P ratio (molar ratio) was 1.63, and the powder was confirmed to be covered with hydroxyapatite.

[0086] Next, 20 g of the obtained apatite-covered powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were mixed and shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the mixture was dried for 5 minutes at a pressure of not greater than 1 MPa and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured powder was passed through a 250 μ m sieve. A 6 g portion of the sifted iron powder was packed into a die with an inner diameter of 14 mm, and molded into a cylindrical tablet at a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 236 $\mu\Omega$ m. The compact density was 7.50 g/cm³. The polished tablet was fired under a nitrogen atmosphere, at 600°C for 1 hour, and after polishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 75 $\mu\Omega$ m. The compact density was 7.50 g/cm³.

[Example 3]

[0087] After adding an ammonium dihydrogenphosphate aqueous solution dropwise to the contents of the 4-necked flask as in Example 2, an additional step of stirring for 1.5 hours in an oil bath at 30°C was carried out.

[0088] Specifically, in a 300 mL 4-necked flask there were placed 75 mL (1.79 mmol, 0.024 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (1.07 mmol, 0.014 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous

solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0089] The oil bath temperature was then raised from 30°C to 90°C over a period of 10 minutes, and reaction was conducted at 90°C for 2 hours while stirring. The obtained slurry was suction filtered and the filtered product was dried in an oven at 110°C to obtain a gray powder. Upon analyzing the atomic abundance ratio near the surface of the obtained powder by XPS, the atomic abundance ratio was Fe: 5.56%, Ca: 14.85% and the Ca/P ratio (molar ratio) was 1.63, and the powder was confirmed to be covered with hydroxyapatite.

[0090] Next, 20 g of the obtained apatite-covered powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were mixed and shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 µm sieve.

After packing 6 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 111 µΩm. The compact density was 7.51 g/cm². The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 55 µΩm. The compact density was 7.51 g/cm².

[Example 4]

[0091] The 90°C reaction time in Example 3 was changed from 2 hours to 10 minutes.

[0092] Specifically, in a 300 mL 4-necked flask there were placed 75 mL (1.79 mmol, 0.024 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (1.07 mmol, 0.014 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0093] The oil bath temperature was then raised from 30°C to 90°C over a period of 10 minutes, and reaction was conducted at 90°C for 10 minutes while stirring. The obtained slurry was then suction filtered and dried in an oven at 110°C to obtain a gray iron powder. Upon analyzing the atomic abundance ratio near the surface of the obtained powder by XPS, the atomic abundance ratio was Fe: 6.79%, Ca: 12.77% and the Ca/P ratio (molar ratio) was 1.44.

[0094] Next, 20 g of the obtained apatite-covered powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 µm sieve. After packing 6 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 214 µΩm. The compact density was 7.50 g/cm². The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 53 µΩm. The compact density was 7.49 g/cm².

[Example 5]

[0095] The reaction time at 90°C in Example 3 was changed from 2 hours to 5 hours.

[0096] Specifically, in a 300 mL 4-necked flask there were placed 75 mL (1.79 mmol, 0.024 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (1.07 mmol, 0.014 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0097] The oil bath temperature was then raised from 30°C to 90°C over a period of 10 minutes, and reaction was conducted at 90°C for 5 hours while stirring. The obtained slurry was suction filtered and dried in an oven at 110°C to obtain a gray iron powder. Upon analyzing the atomic abundance ratio near the surface of the obtained powder by XPS, the atomic abundance ratio was Fe: 6.07%, Ca: 13.98% and the Ca/P ratio was 1.67, and the powder was confirmed to be covered with hydroxyapatite.

[0098] Next, 20 g of the obtained apatite-covered powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 μm sieve. After packing 6 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 218 $\mu\Omega\text{m}$. The compact density was 7.47 g/cm². The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 93 $\mu\Omega\text{m}$. The compact density was 7.47 g/cm².

[Example 6]

[0099] The reaction temperature of 90°C in Example 3 was changed to 30°C.

[0100] Specifically, in a 300 mL 4-necked flask there were placed 75 mL (1.79 mmol, 0.024 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (1.07 mmol, 0.014 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 3.5 hours while keeping the temperature of the oil bath at 30°C.

[0101] The obtained slurry was then suction filtered and dried in an oven at 110°C to obtain a gray iron powder. Upon analyzing the atomic abundance ratio near the surface of the obtained powder by XPS, the atomic abundance ratio was Fe: 7.84%, Ca: 11.67% and the Ca/P ratio (molar ratio) was 1.65, and the iron powder was confirmed to be covered with hydroxyapatite.

[0102] Next, 20 g of the obtained apatite-covered powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 μm sieve. After packing 6 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 119 $\mu\Omega\text{m}$. The compact density was 7.53 g/cm². The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 31 $\mu\Omega\text{m}$. The density was 7.53 g/cm².

[Example 7]

[0103] The reaction temperature of 90°C in Example 3 was changed to 50°C. Specifically, in a 300 mL 4-necked flask there were placed 75 mL (1.79 mmol, 0.024 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (1.07 mmol, 0.014 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0104] The oil bath temperature was then raised from 30°C to 50°C over a period of 5 minutes, and reaction was conducted at 90°C for 2 hours while stirring. The obtained slurry was suction filtered and dried in an oven at 110°C to obtain a gray iron powder. Upon analyzing the atomic abundance ratio near the surface of the obtained powder by XPS, the atomic abundance ratio was Fe: 7.08%, Ca: 13.24% and the Ca/P ratio (molar ratio) was 1.77, and the iron powder

was confirmed to be covered with hydroxyapatite.

[0105] Next, 20 g of the obtained apatite-covered powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 μm sieve.

[0106] After packing 6 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 176 $\mu\Omega\text{m}$. The compact density was 7.46 g/cm³. The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 53 $\mu\Omega\text{m}$. The compact density was 7.47 g/cm³.

[Example 8]

[0107] The reaction temperature of 90°C in Example 3 was changed to 30°C, and firing at 110°C was not carried out.

[0108] Specifically, in a 300 mL 4-necked flask there were placed 75 mL (1.79 mmol, 0.024 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (1.07 mmol, 0.014 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 3.5 hours while keeping the temperature of the oil bath at 30°C.

[0109] The obtained slurry was then suction filtered, removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa to obtain a gray iron powder. Upon analyzing the atomic abundance ratio near the surface of the obtained powder by XPS, the atomic abundance ratio was Fe: 5.53%, Ca: 13.63% and the Ca/P ratio (molar ratio) was 1.52.

[0110] Next, 20 g of the obtained apatite-covered powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 μm sieve.

After packing 6 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 168 $\mu\Omega\text{m}$. The compact density was 7.50 g/cm³. The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after polishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 56 $\mu\Omega\text{m}$. The compact density was 7.49 g/cm³.

[Example 9]

[0111] The reaction temperature of 90°C in Example 3 was changed to 50°C, and firing at 110°C was not carried out.

[0112] Specifically, in a 300 mL 4-necked flask there were placed 75 mL (1.79 mmol, 0.024 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (1.07 mmol, 0.014 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0113] The oil bath temperature was then raised from 30°C to 50°C over a period of 5 minutes, and the contents of the 4-necked flask were reacted at 90°C for 2 hours while stirring. The obtained slurry was then suction filtered, removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa to obtain a gray iron powder. Upon analyzing the atomic abundance ratio near the surface of the obtained powder by XPS, the atomic abundance ratio was Fe: 4.89%, Ca: 15.54% and the Ca/P ratio (molar ratio) was 1.77, and the powder was confirmed to be covered

with hydroxyapatite.

[0114] Next, 20 g of the obtained apatite-covered powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 μm sieve. After packing 6 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 137 $\mu\Omega\text{m}$. The compact density was 7.50 g/cm³. The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 44 $\mu\Omega\text{m}$. The compact density was 7.50 g/cm³.

[Example 10]

[0115] The firing at 110°C in Example 3 was not carried out.

[0116] Specifically, in a 300 mL 4-necked flask there were placed 75 mL (1.79 mmol, 0.024 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (1.07 mmol, 0.014 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0117] The oil bath temperature was then raised from 30°C to 90°C over a period of 10 minutes, and reaction was conducted at 90°C for 2 hours while stirring. The obtained slurry was suction filtered and vacuum dried at 0 MPa to obtain a gray iron powder. Upon analyzing the obtained iron powder by XPS, the atomic abundance ratio was Fe: 3.85%, Ca: 16.63% and the Ca/P ratio (molar ratio) was 1.56.

[0118] Next, 20 g of the obtained apatite-covered powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 μm sieve. After packing 6 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 137 $\mu\Omega\text{m}$. The compact density was 7.50 g/cm³. The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 30 $\mu\Omega\text{m}$. The compact density was 7.50 g/cm³.

[Example 11]

[0119] In Example 3, the calcium nitrate charging amount was changed from 1.79 mmol to 0.60 mmol and the ammonium dihydrogenphosphate charging amount was changed from 1.07 mmol to 0.36 mmol.

[0120] Specifically, in a 300 mL 4-necked flask there were placed 75 mL (0.60 mmol, 0.008 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (0.36 mmol, 0.005 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0121] The oil bath temperature was then raised from 30°C to 90°C over a period of 10 minutes, and reaction was conducted at 90°C for 2 hours while stirring. The obtained slurry was suction filtered and dried in an oven at 110°C to obtain a gray iron powder. Upon analyzing the atomic abundance ratio near the surface of the obtained powder by XPS, the atomic abundance ratio was Fe: 7.29%, Ca: 13.14% and the Ca/P ratio (molar ratio) was 1.52.

[0122] Next, 20 g of the obtained apatite-covered powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL,

and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 μm sieve. After packing 6 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 122 $\mu\Omega\text{m}$. The compact density was 7.56 g/cm². The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 30 $\mu\Omega\text{m}$. The compact density was 7.56 g/cm².

[Example 12]

[0123] In Example 3, the calcium nitrate charging amount was changed from 1.78 mmol to 2.98 mmol and the ammonium dihydrogenphosphate charging amount was changed from 1.07 mmol to 1.78 mmol.

[0124] Specifically, in a 300 mL 4-necked flask there were placed 75 mL (2.98 mmol, 0.040 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (1.78 mmol, 0.024 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0125] The oil bath temperature was then raised from 30°C to 90°C over a period of 10 minutes, and reaction was conducted at 90°C for 2 hours while stirring. The obtained slurry was suction filtered and dried in an oven at 110°C to obtain a gray iron powder. Upon analyzing the atomic abundance ratio near the surface of the obtained powder by XPS, the atomic abundance ratio was Fe: 2.76%, Ca: 17.59% and the Ca/P ratio (molar ratio) was 1.67.

[0126] Next, 20 g of the obtained apatite-covered powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 μm sieve. After packing 6 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 213 $\mu\Omega\text{m}$. The compact density was 7.44 g/cm². The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 88 $\mu\Omega\text{m}$. The compact density was 7.44 g/cm².

[Example 13]

[0127] Hydroxyapatite-covered iron powder with a hydroxyapatite layer composed of a single layer was prepared in the same manner as Example 11, and the same treatment was also repeated to prepare hydroxyapatite-covered iron powder with a hydroxyapatite layer composed of a two-layer structure.

[0128] Specifically, in a 300 mL 4-necked flask there were placed 75 mL (0.60 mmol, 0.008 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (0.36 mmol, 0.005 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise thereto over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0129] The oil bath temperature was then raised from 30°C to 90°C over a period of 1.0 minutes, and the contents of the 4-necked flask were reacted at 90°C for 2 hours while stirring. The obtained slurry was suction filtered and dried in an oven at 110°C to obtain a gray iron powder (yield: 96 mass%).

[0130] Next, 28.8 g of the obtained apatite single-layer-covered powder and 72 mL (0.57 mmol, 0.008 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water were placed in a 300 mL 4-necked flask, and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 72 mL (0.34 mmol, 0.005 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping

funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise thereto over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0131] The oil bath temperature was then raised from 30°C to 90°C over a period of 10 minutes, and reaction was conducted at 90°C for 2 hours while stirring. The obtained slurry was suction filtered and dried in an oven at 110°C to obtain a gray iron powder. Upon analyzing the atomic abundance ratio near the surface of the obtained powder by XPS, the atomic abundance ratio was Fe: 7.05%, Ca: 13.84% and the Ca/P ratio (molar ratio) was 1.59.

[0132] Next, 20 g of the obtained apatite two-layer-covered powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 μm sieve. After packing 6 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 131 $\mu\Omega\text{m}$. The compact density was 7.53 g/cm². The polished tablet was fired under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 59 $\mu\Omega\text{m}$. The compact density was 7.53 g/cm².

[Example 14]

[0133] Hydroxyapatite-covered iron powder with a hydroxyapatite layer composed of two layers was prepared in the same manner as Example 13, and the same treatment was also repeated to prepare hydroxyapatite-covered iron powder with a hydroxyapatite layer composed of a three-layer structure.

[0134] Specifically, in a 300 mL 4-necked flask there were placed 75 mL (0.60 mmol, 0.008 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 30 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.), and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 75 mL (0.36 mmol, 0.005 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0135] The oil bath temperature was then raised from 30°C to 90°C over a period of 10 minutes, and reaction was conducted at 90°C for 2 hours while stirring. The obtained slurry was suction filtered and dried in an oven at 110°C to obtain a gray iron powder.

[0136] Next, 29.5 g of the obtained apatite single-layer-covered iron powder and 74 mL (0.59 mmol, 0.008 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water were placed in a 300 mL 4-necked flask, and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 74 mL (0.35 mmol, 0.005 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0137] The oil bath temperature was then raised from 30°C to 90°C over a period of 10 minutes, and the contents of the 4-necked flask were reacted at 90°C for 2 hours while stirring. The obtained slurry was suction filtered and dried in an oven at 110°C to obtain a gray iron powder.

[0138] A 29.5 g portion of the obtained apatite two-layer-covered iron powder and 74 mL (0.59 mmol, 0.008 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water were placed in a 300 mL 4-necked flask, and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 74 mL (0.35 mmol, 0.005 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 10 minutes, after which the mixture was stirred for 1.5 hours while keeping the temperature of the oil bath at 30°C.

[0139] The oil bath temperature was then raised from 30°C to 90°C over a period of 10 minutes, and reaction was conducted at 90°C for 2 hours while stirring. The obtained slurry was suction filtered and dried in an oven at 110°C to obtain a gray iron powder. Upon analyzing the atomic abundance ratio near the surface of the obtained powder by XPS,

the atomic abundance ratio was Fe: 10.33%, Ca: 10.95% and the Ca/P ratio (molar ratio) was 1.69.

[0140] Next, 20 g of the obtained apatite three-layer-covered iron powder and 2 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 μm sieve. After packing 6 g of the obtained nanosilica-attached apatite three-layer-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 95 $\mu\Omega\text{m}$. The compact density was 7.494 g/cm³. The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 31 $\mu\Omega\text{m}$. The compact density was 7.50 g/cm³.

[Example 15]

[0141] The amount of iron powder charged in Example 3 was changed to a 33-fold amount, the reactor volume and amount of solvent were correspondingly changed 33-fold, and the time for stirring in the 30°C oil bath after dropwise addition of the ammonium dihydrogenphosphate aqueous solution to the 4-necked flask contents was changed from 1.5 hours to 2 hours.

[0142] Specifically, 250 mL (5.95 mmol, 0.024 M) of a calcium nitrate aqueous solution prepared to pH 11 or higher with 25% ammonia water and 100 g of iron powder (pure iron powder 300NH, by Kobe Steel, Ltd.) were placed in a 1000 mL 4-necked flask, and the mixture was stirred for 15 minutes in an oil bath at 30°C. Next, 250 mL (3.57 mmol, 0.014 M) of an ammonium dihydrogenphosphate aqueous solution prepared to pH 11 or higher with 25% ammonia water was placed in a dropping funnel with a bypass line and the funnel was attached to the 4-necked flask. The contents of the 4-necked flask were stirred in the oil bath at 30°C, while adding the ammonium dihydrogenphosphate aqueous solution in the dropping funnel dropwise over a period of 30 minutes, after which the mixture was stirred for 2 hours while keeping the temperature of the oil bath at 30°C.

[0143] The oil bath temperature was then raised from 30°C to 90°C over a period of 10 minutes, and reaction was conducted at 90°C for 2 hours while stirring. The obtained slurry was suction filtered and dried in an oven at 110°C to obtain a gray iron powder. Upon analyzing the obtained iron powder by XPS, the atomic abundance ratio was Fe: 3.85%, Ca: 15.30% and the Ca/P ratio was 1.76, and the iron powder was confirmed to be covered with hydroxyapatite.

[0144] Also, 60 g of the obtained apatite-covered iron powder and 6 g of an organosilica sol-toluene solution (solid concentration: 3.0 mass%) were shaken for 10 minutes in a polypropylene bottle with a maximum internal volume of 50 mL, and then the contents were removed into a stainless steel dish and dried for 5 minutes at a pressure of not greater than 1 MPa, and the removed powder was pre-cured at 200°C for 25 minutes. The pre-cured iron powder was passed through a 250 μm sieve. After packing 6 g of the obtained nanosilica-attached apatite-covered iron powder into a die with an inner diameter of 14 mm, it was molded into a cylindrical tablet with a molding pressure of 1000 MPa/cm². The thickness of the obtained tablet was approximately 5 mm. The surface of the molded tablet was polished, and the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 193 $\mu\Omega\text{m}$. The compact density was 7.51 g/cm³. The polished tablet was annealed under a nitrogen atmosphere, at 600°C for 1 hour, and after repolishing the surface, the volume resistivity (resistivity) was measured with a four-terminal resistivity meter to be 41 $\mu\Omega\text{m}$. The compact density was 7.51 g/cm³.

[0145] The evaluation results for the hydroxyapatite-covered iron powders and nanosilica-attached hydroxyapatite-covered iron powders obtained in Examples 1-15 are summarized in Tables 3 to 5.

[0146]

[Table 3]

Examples	Apatite starting material charging amount (with respect to iron powder) (mass%)	Synthesis conditions				
		Apatite-covered iron powder synthesis step				Nanosilica-attached apatite-coated iron powder synthesis step
		Iron powder mass (g)	Synthesis time @30°C (min)	Synthesis time @T°C (min)	Drying @ 110°C	Drying @200°C ..
Example 1	0.6	30	0	120(T=90)	Conducted	Conducted
Example 2	0.6	30	25	120(T=90)	Conducted	Conducted
Example 3	0.6	30	115	120(T=90)	Conducted	Conducted
Example 4	0.6	30	115	10(T=90)	Conducted	Conducted
Example 5	0.6	30	115	300(T=90)	Conducted	Conducted
Example 6	0.6	30	235	0	Conducted	Conducted
Example 7	0.6	30	115	120(T=50)	Conducted	Conducted
Example 8	0.6	30	25	0	None	Conducted
Example 9	0.6	30	115	120(T=50)	None	Conducted
Example 10	0.6	30	115	120(T=90)	None	Conducted
Example 11	0.2	30	115	120(T=90)	Conducted	Conducted
Example 12	1.0	30	115	120(T=90)	Conducted	Conducted
Example 13	0.6(×2)	30	115(×2)	120(T=90) (×2)	Conducted	Conducted
Example 14	0.6(×3)	30	115(×3)	120(T=90) (×3)	Conducted	Conducted
Example 15	0.6	100	165	120(T=90)	Conducted	Conducted

[0147]

[Table 4]

Examples	XPS data (atomic ratios, %)						Coverage factor O1s+Ca2p+P2p / (O1s+Ca2p+Fe2p+P2p) × 100	Ca/P
	C1s	N1s	O1s	Ca2p	Fe2p	P2p		
Example 1	16.7	0	53.5	15.7	4.6	9.6	94.5	1.67
Example 2	13.9	0	55.2	17.1	3.3	10.5	96.2	1.63
Example 3	14.1	0	56.4	14.9	5.6	9.1	93.5	1.63
Example 4	14.5	0	57.0	12.8	6.9	8.9	92.1	1.43
Example 5	14.0	0	57.6	14.0	6.1	8.4	92.9	1.67
Example 6	16.3	0	57.1	11.7	7.8	7.1	90.6	1.65
Example 7	15.1	0	57.2	13.2	7.1	7.5	91.7	1.77
Example 8	16.8	0	55.1	13.6	5.5	8.9	93.4	1.52
Example 9	12.3	0	58.5	15.5	4.9	8.8	94.4	1.77
Example 10	11.0	0	57.9	16.6	3.9	10.6	95.7	1.56

(continued)

Examples	XPS data (atomic ratios, %)						Coverage factor O1s+Ca2p+P2p / (O1s+Ca2p+Fe2p+P2p) × 100	Ca/P
	C1s	N1s	O1s	Ca2p	Fe2p	P2p		
Example 11	15.7	0	55.2	13.1	7.3	8.7	91.4	1.52
Example 12	11.1	0	58.0	17.6	2.8	10.5	96.9	1.67
Example 13	13.6	0	56.8	13.8	7.1	8.7	91.8	1.59
Example 14	14.6	0	57.7	11.0	10.3	6.5	87.9	1.69
Example 15	16.3	0	55.9	15.3	3.9	8.7	95.4	1.76

[0148]

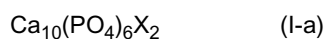
[Table 5]

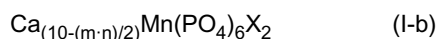
Examples	Powder magnetic core properties	
	Compact density (g/cm ³)	Resistivity (μΩm)
Example 1	7.47	91
Example 2	7.50	75
Example 3	7.51	55
Example 4	7.49	53
Example 5	7.47	93
Example 6	7.53	31
Example 7	7.47	53
Example 8	7.48	56
Example 9	7.50	44
Example 10	7.50	30
Example 11	7.56	30
Example 12	7.44	88
Example 13	7.53	59
Example 14	7.50	31
Example 15	7.51	41

[0149] Judging from Table 4, hydroxyapatite layers could be formed on the metal powders with the similar coverage factor regardless of the synthesis method. Also, judging from Tables 3 and 5, powder magnetic cores of the nanosilica-attached hydroxyapatite-covered iron powders obtained using a step of pre-curing at 100-300°C in the production process exhibited high resistivity and compact density.

Claims

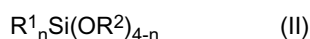
1. A powder comprising metal powder, an apatite layer covering the metal powder and silica particles attached to the metal powder or apatite layer.
2. The powder according to claim 1, wherein the apatite layer contains a compound represented by the following formula (I-a) or (I-b).





(In the formulas, M represents a cation-donating atom, m represents the valency of the cation donated by M, n is greater than 0 and not greater than 5, and X represents an atom or group of atoms that donates a monovalent anion.)

3. The powder according to claim 1 or 2, wherein the silica particles are silica particles that have been surface-modified with an organic group.
4. The powder according to claim 3, wherein the silica particles that have been surface-modified with an organic group are silica particles that have been surface-modified using a compound represented by the following formula (II) or (III).



(In the formulas, n is an integer of 1-3, R¹ and R² represent monovalent organic groups, and X represents a halogen.)

5. The powder according to any one of claims 1 to 4, wherein the metal powder is a soft magnetic material powder.
6. The powder according to any one of claims 1 to 5, which is a powder for a powder magnetic core.
7. A method for producing powder comprising:

a first step of covering metal powder with apatite to obtain apatite-covered metal powder,
 a second step of attaching silica powder to the metal powder surface or apatite layer surface of the apatite-covered metal powder obtained in the first step, and
 a third step of pre-curing the powder obtained in the second step at not greater than 350°C to obtain powder comprising the metal powder, the apatite layer covering the metal powder, and silica particles attached to the metal powder or apatite layer.

8. The method for producing powder according to claim 7, wherein phosphated metal powder is used as the metal powder provided in the first step.

Fig.1

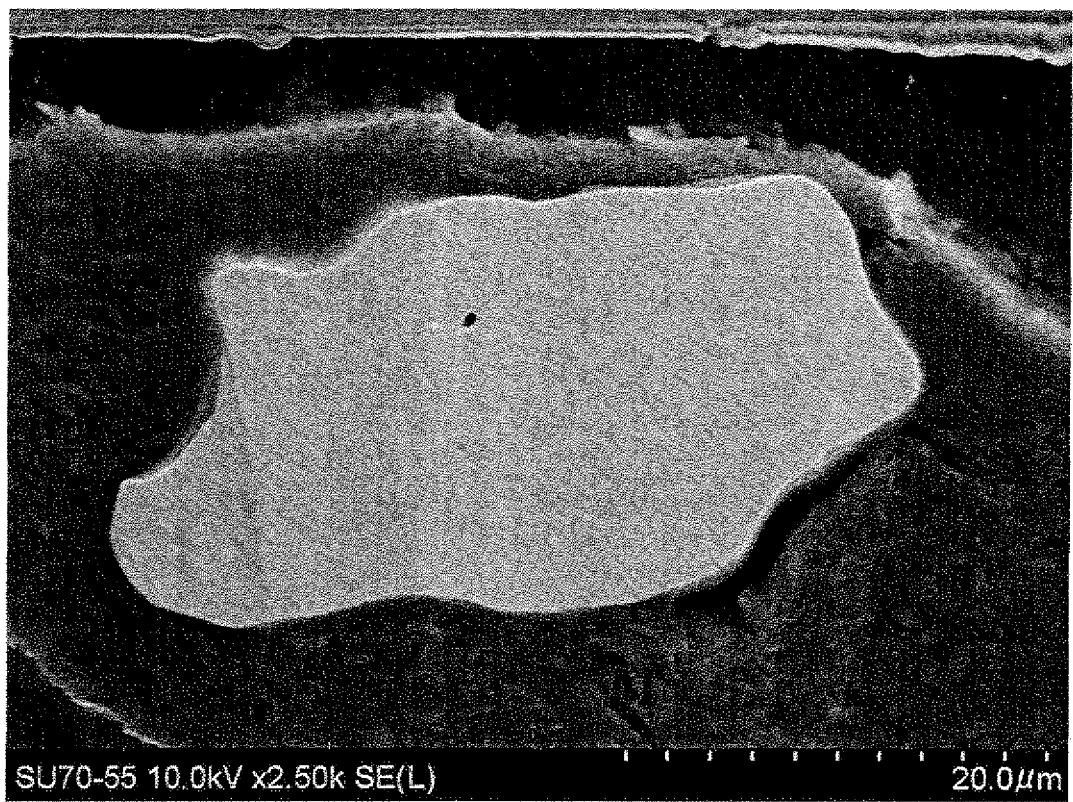


Fig.2

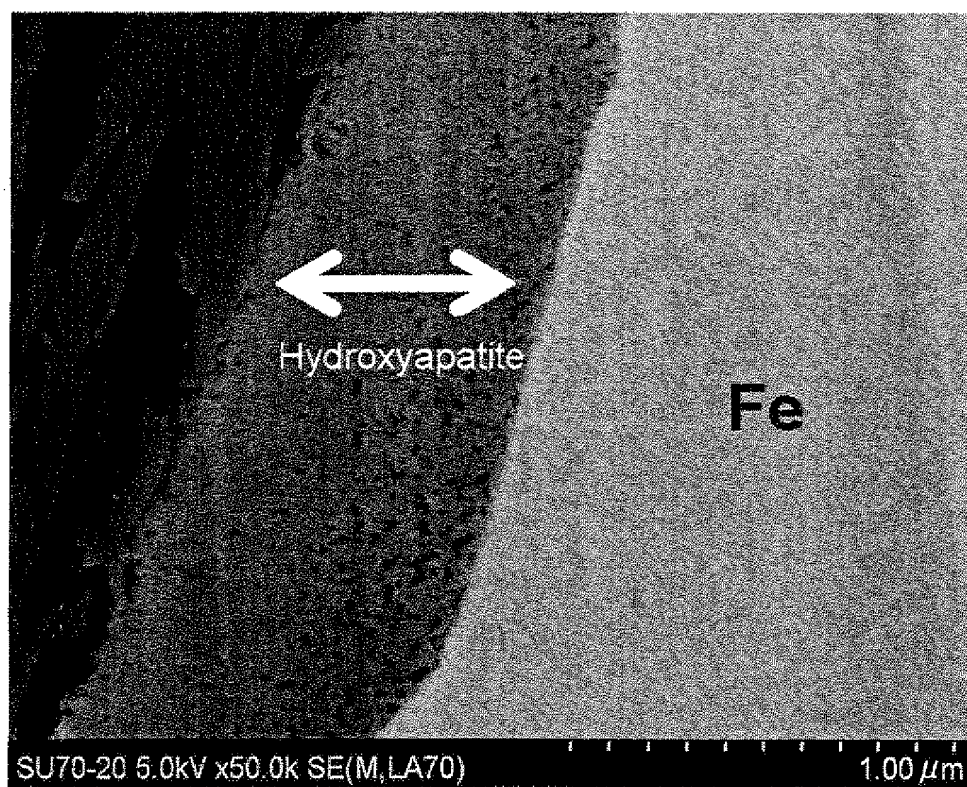


Fig.3

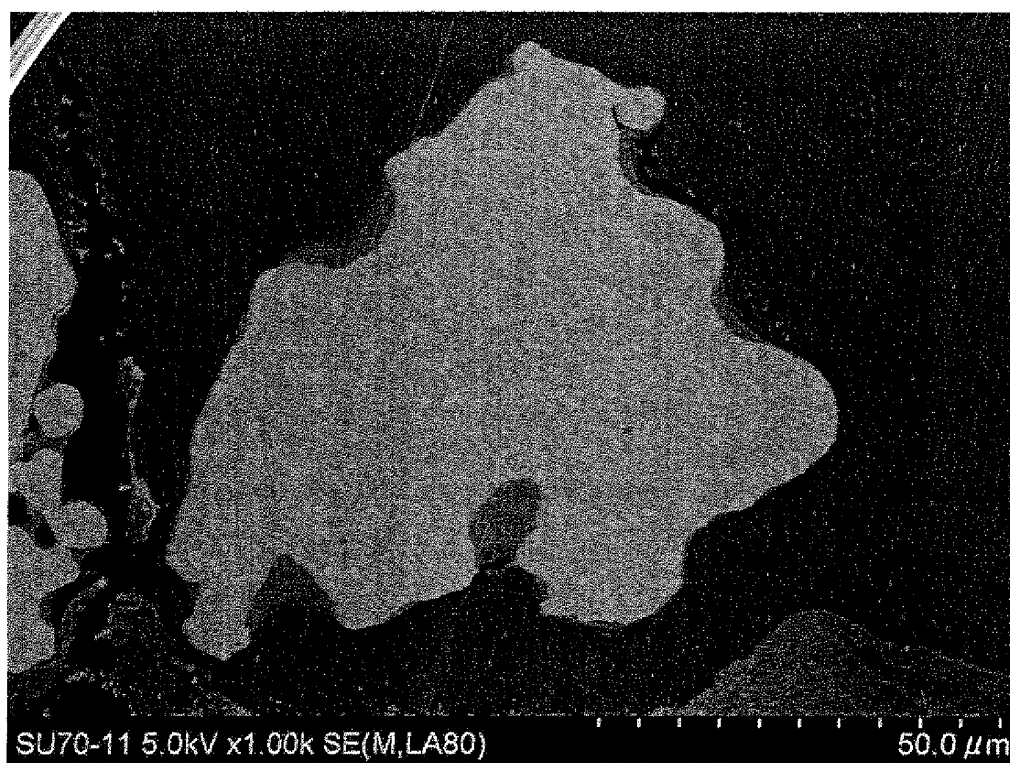
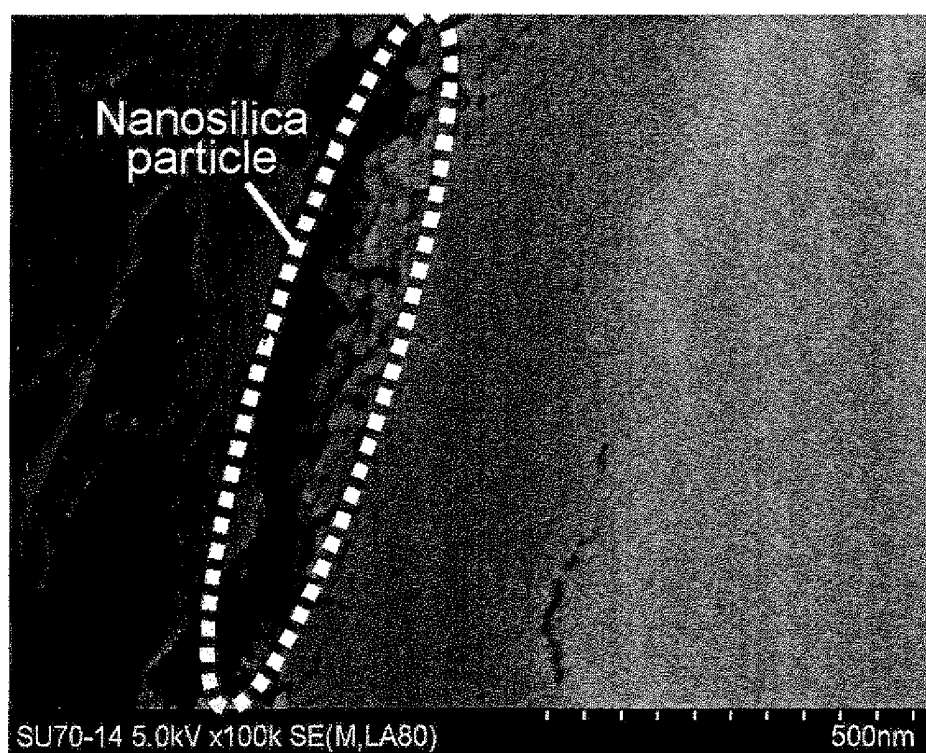


Fig.4



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2008/071031

A. CLASSIFICATION OF SUBJECT MATTER

B22F1/02(2006.01)i, B22F1/00(2006.01)i, H01F1/24(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)

B22F1/00-1/02, H01F1/24

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

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	Toshitaka ISHIZAKI et al., "Silica Nanosheet Coat-ho ni yoru Appun Jishin'yo Shinki Zetsuen Himaku no Kaihatsu", The Japan Institute of Metals Koen Gaiyo, Vol.137, The Japan Institute of Metals, 28 September, 2005 (28.09.05), page 481	1-8
A	JP 2003-282316 A (Toyota Central Research and Development Laboratories, Inc.), 03 October, 2003 (03.10.03), Claim 2; examples & US 2003/0230362 A1	1-8
A	JP 2006-348335 A (JFE Steel Corp.), 28 December, 2006 (28.12.06), Claim 1 (Family: none)	1-8

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

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Date of the actual completion of the international search
02 February, 2009 (02.02.09)Date of mailing of the international search report
10 February, 2009 (10.02.09)Name and mailing address of the ISA/
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