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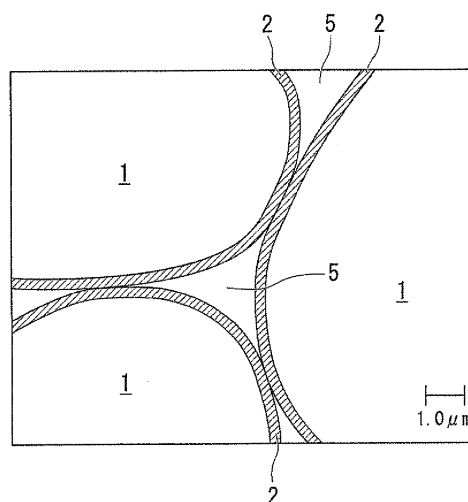
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(54) **HIGH-STRENGTH SOFT-MAGNETIC COMPOSITE MATERIAL OBTAINED BY COMPACTION/ BURNING AND PROCESS FOR PRODUCING THE SAME**

(57) The present invention relates to a soft-magnetic composite material obtained by compaction and heat treatment. This material is produced by mixing and compacting Mg-containing oxide-coated soft-magnetic particles with at least one type of silicone resin, low melting glass and metal oxide, and heat treatment in a non-oxidizing atmosphere to obtain a precursor of a soft-magnetic composite compaction-heat treated material, followed by heat-treating in an oxidizing atmosphere to obtain a heat treated body.

FIG. 1B



Description

TECHNICAL FIELD

[0001] The present invention relates to a high-strength soft-magnetic composite material obtained by compaction and heat treatment, which is used as a material of various types of electromagnetic circuit components of motors, actuators, reactors, transformers, choke cores, magnetic sensor cores or the like, and to a production method thereof. The present application claims priority on Japanese Patent Application No. 2007-289774, filed on November 7, 2007, the content of which is incorporated herein by reference.

BACKGROUND ART

[0002] As materials for magnetic cores of motors, actuators, magnetic sensors, or the like, soft-magnetic sintered materials produced by sintering iron powder, Fe-Al iron-based soft-magnetic alloy powder, Fe-Ni iron-based soft-magnetic alloy powder, Fe-Cr iron-based soft-magnetic alloy powder, Fe-Si iron-based soft-magnetic alloy powder and Fe-Si-Al iron-based soft-magnetic alloy powder (referred as soft-magnetic metal particles hereinafter) have conventionally been known. Although this type of soft-magnetic sintered material has high magnetic flux density, it has the problem of having a low specific electrical resistance and hence poor high frequency characteristics. To improve the high frequency characteristics by increasing the specific electrical resistance, it has been proposed using soft-magnetic materials or the like that are bonded by water glass or low melting glass (see Patent Document 1 or Patent Document 2).

[0003] One of a problem of the above-mentioned approach is that the soft magnetic metal particles adhere poorly to the water glass or low melting glass, in the composite soft magnetic sintered materials. To achieve sufficient mechanical strength in this composite soft magnetic heat treated materials, a large amount of water glass or low melting glass, which is enough to disperse the soft-magnetic metal particles, is needed to be incorporated. Although a high specific electrical resistance can be achieved with the compacted soft-magnetic materials produced by using a large amount of water glass or low melting glass, magnetic flux density is significantly reduced. As a result, they are not useful as materials for the magnetic cores of motors, actuators and magnetic sensors.

[0004] To achieve high magnetic flux density and high specific electrical resistance at the same time, it has been proposed using a composite soft-magnetic sintered material including a soft-magnetic metal particle phase and a grain boundary phase surrounding the soft-magnetic metal particle phase, wherein the grain boundary phase includes a ZnO phase having the hexagonal crystal structure, an Fe and Zn mixed oxide phase having the cubic crystal structure, and a glass phase (see Patent Document 3). The ZnO phase having the hexagonal crystal structure is dispersed contacting to the soft-magnetic metal particle phase. The Fe and Zn mixed oxide phase having the cubic crystal structure is dispersed contacting to the ZnO phase. The glass phase is dispersed in between the Fe and Zn mixed oxide phases having the cubic crystal structure, and contacting with the Fe and Zn mixed oxide phase.

As an alternative, a method for producing compacted magnetic materials comprising, mixing Mg-containing iron powders coated with a Mg-containing ferrite film deposited by a chemical method such as chemical plating or a coating method, with low melting glass powders, molding by compaction, and heating, is known (see Patent Document 4).

Patent Document 1: Japanese Unexamined Patent Application, First Publication No. H5-258934
 Patent Document 2: Japanese Unexamined Patent Application, First Publication No. S63-158810
 Patent Document 3: Japanese Unexamined Patent Application, First Publication No. 2004-253787
 Patent Document 4: Japanese Unexamined Patent Application, First Publication No. 2004-297036

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0005] One of the problems in the composite soft-magnetic sintered material described in Patent Document 3, is that the mixed oxide phase including Fe and Zn decomposes if it was heated at a temperature higher than 600°C. If the heat treatment was performed at 600°C or lower temperature, glass powders would not be melted, and thereby making it difficult to enhance adhesion between the soft-magnetic metal particle phases and hindering production of a high-strength soft-magnetic composite compaction-heat treated material.

In addition, when glass powder is added to and mixed with zinc oxide-coated soft-magnetic metal particles followed by molding, the coating with zinc oxide becomes more susceptible to damages caused by friction between the glass powder and the zinc oxide coating (insulating layer), making it difficult to produce a soft-magnetic composite compaction-heat treated material having high specific electrical resistance.

[0006] In the method that the soft-magnetic composite compaction-heat treated material is obtained by compaction

and heat treatment Mg-containing iron oxide-coated iron powders, the surface of the soft-magnetic metal particles is coated with Mg-containing ferrite film by a chemical method. This chemically formed ferrite film is not stable and subjected to transformation, resulting reduction of insulating properties and poor adherence of the film to the surface of soft-magnetic metal particles. Therefore, even if the Mg-containing iron oxide-coated powder is press-formed with low melting glass followed by heat treatment, it does not guarantee reliable production of a high-strength soft-magnetic composite compaction-heat treated material.

[0007] In consideration of the problems described above, an object of the present invention is to provide a high-strength soft-magnetic composite material by compaction and heat treatment, which can be subjected to a stress-relief annealing process retaining a high specific electrical resistance and low coercivity. It is achieved by an MgO coating that has high heat resistance properties, allowing a heat treatment process at a temperature higher than 600°C, for example at 700°C. In addition, another object of the present invention is to provide a high-strength soft-magnetic composite material by compaction and heat treatment, which has high bending strength. It is achieved by forming strong bonding between soft-magnetic metal particles by filling the interface connecting the soft-magnetic metal particles with a grain boundary layer of low melting glass or metal oxide containing iron oxide mainly consisted of Fe_3O_4 .

Means for Solving the Problems

[0008] The inventors of the present invention conducted a research on Fe-based soft-magnetic sintered materials, and found that an insulating film of an Mg-containing oxide-coated soft-magnetic powder is not susceptible to damages during press forming process.

In the present invention, an oxidized soft-magnetic powder having an iron oxide film on the surface of the soft-magnetic powder is prepared by preheating Fe-based soft-magnetic powders in an oxidizing atmosphere. After addition of Mg powders to the oxidized soft-magnetic powders, and mixing them with a rolling granulation agitation mixer, the mixed powders are heated in an inert gas atmosphere or vacuum atmosphere. If it is needed, further oxidation treatment is carried out by heating in an oxidizing atmosphere. According to this invention, a Mg-Fe-O ternary oxide deposition film containing at least (Mg, Fe)O as oxides among ones found in the Mg-Fe-O ternary system which are typified by (Mg, Fe)O and $(\text{Mg, Fe})_3\text{O}_4$ in the conventionally known MgO-FeO- Fe_2O_3 system, can be formed on the surface of a soft-magnetic powder particles.

[0009] Far superior adherence of the oxide film to the Fe-based soft-magnetic powder, compared with the conventional materials, can be achieved when the Mg-Fe-O ternary oxide deposition film containing at least (Mg, Fe)O, is formed on the surface of the Mg-containing oxide-coated soft-magnetic powder. Because of the superior adherence of the oxide film, the insulating oxide film became less susceptible to damages during press forming of the Mg-containing oxide-coated soft-magnetic powder. Since the oxide film stays between the individual Fe-based soft-magnetic powders properly, there is no decrease in insulating properties of the oxide film even if high-temperature stress-relief heat treatment is carried out after press forming. As a consequence, a high specific electrical resistance can be achieved, leading to a reduced level of the eddy current loss. Furthermore, due to low coercivity even after stress-relief heat treatment, hysteresis loss can be held to a low level also. Thus, a soft-magnetic composite compaction-heat treated material with low hysteresis loss can be produced.

The inventors of the present invention focused on this technology, conducting research on compacted materials produced by compaction molding the Mg-containing oxide-coated soft-magnetic powder, thereby leading to completion of the present invention.

[0010]

(1) A high-strength soft-magnetic composite material obtained by compaction and heat treatment as defined in a first aspect of the present invention is a high-strength soft-magnetic composite material obtained by compaction and heat treatment in which a plurality of Mg-containing oxide-coated soft-magnetic particles bonded each other through an interposing grain boundary layer, wherein the Mg-containing oxide-coated soft-magnetic particles are provided with Fe-based soft-magnetic particles and an Mg-containing oxide film coated on the surface of the soft-magnetic metal particles, and the high-strength soft-magnetic composite material obtained by compaction and heat treatment is provided with a surface layer portion in which a plurality of the Mg-containing oxide-coated soft-magnetic particles are bonded each other through an interposing surface side grain boundary layer that mainly consists of at least one type of silicon oxide containing iron oxide consisting mainly of Fe_3O_4 or FeO and iron oxide containing Mg, and an inner layer portion in which a plurality of the Mg-containing oxide-coated soft-magnetic particles are bonded each other through an interposing inside grain boundary layer that mainly consists of at least one type of silicon oxide and Mg-containing iron oxide.

(2) A high-strength soft-magnetic composite material obtained by compaction and heat treatment as defined in a second aspect of the present invention is the high-strength soft-magnetic composite material obtained by compaction and heat treatment described in item (1), wherein bonds between the plurality of the Mg-containing oxide-coated

soft-magnetic particles through the interposing grain boundary layer are formed by performing mixing, compacting and heat treatments in which the Mg-containing oxide-coated soft-magnetic particles, which comprise the soft-magnetic metal particles and the Mg-containing oxide film coated on the surface of the soft-magnetic particles are mixed with at least one selected from a group consisting of silicone resin, low melting glass and metal oxide, and the mixed materials are compacted and thereafter the compacted materials are heat treated, the Fe_3O_4 or FeO in the surface side grain boundary layer between the Mg-containing oxide-coated soft-magnetic particles is dispersed and grown by precipitation of an Fe component from the Fe-based soft-magnetic metal particles at a grain boundary in the form of an oxide, and the Mg-containing oxide film adjacent to the surface side grain boundary layer is obtained from an Mg-containing oxide coating film in the Mg-containing oxide-coated soft-magnetic particles before the mixing, compacting and heat treatments.

[0011]

(3) A high-strength soft-magnetic composite material obtained by compaction and heat treatment as defined in another aspect of the present invention is the high-strength soft-magnetic composite material obtained by compaction and heat treatment described in item (1) or (2), wherein the Mg-containing oxide film includes mainly $(\text{Mg}, \text{Fe})\text{O}$, and the low melting glass includes any of $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{SnO-P}_2\text{O}_5$, $\text{SiO}_2\text{-B}_2\text{O}_3\text{-ZnO}$, $\text{SiO}_2\text{-B}_2\text{O}_3\text{-R}_2\text{O}$ and $\text{Li}_2\text{O-ZnO}$.

(4) A high-strength soft-magnetic composite material obtained by compaction and heat treatment as defined in another aspect of the present invention is the high-strength soft-magnetic composite material obtained by compaction and heat treatment described in any of items (1) to (3), wherein the Mg-containing oxide film includes mainly $(\text{Mg}, \text{Fe})\text{O}$, and the metal oxide includes one or more than two metal oxides selected from a group consisting of Al_2O_3 , B_2O_3 , Sb_2O_3 and MoO_3 .

(5) A method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment as defined in another aspect of the present invention is comprised of mixing an Mg-containing oxide-coated soft-magnetic particles, which are provided with Fe-based soft-magnetic metal particles and an Mg-containing oxide film coated on the surface of the soft-magnetic metal particles, with at least one selected from a group consisting of silicone resin, low melting glass, and metal oxide, compacting the mixed materials, and heat treatment the compacted materials in a non-oxidizing atmosphere to obtain a precursor of a soft-magnetic composite compaction-heat treated material, followed by heat-treating in an oxidizing atmosphere; wherein the heat treated material is provided with a surface layer portion on the surface of the precursor in which a plurality of the Mg-containing oxide-coated soft-magnetic particles are bonded each other through an interposing surface side grain boundary layer including a silicon oxide filler containing iron oxide at least consisting mainly of Fe_3O_4 or FeO , or an iron oxide filler at least containing Mg, and the heat treated material is provided with an inner layer portion on the inside layer of the precursor in which a plurality of the Mg-containing oxide-coated soft-magnetic particles are bonded each other through an interposing inside grain boundary layer consisting of mainly at least one kind of iron oxide containing silicon oxide and iron oxide containing Mg.

(6) A method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment as defined in another aspect of the present invention is the production method of described in item (5), wherein the iron oxide in the grain boundary layer between the Mg-containing oxide-coated soft-magnetic particles of the surface layer portion is dispersed and grown by precipitation of an Fe component from the Fe-based soft-magnetic metal particles at a grain boundary in the form of an oxide.

[0012]

(7) A method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment as defined in another aspect of the present invention is the production method described in item (5) or (6), wherein the non-oxidizing atmosphere is an inert gas atmosphere, such as a nitrogen gas atmosphere, argon gas atmosphere, or a hydrogen gas atmosphere.

(8) A method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment as defined in another aspect of the present invention is the production method described in any of items (5) to (7), wherein the oxidizing atmosphere is a steam or air atmosphere in a temperature range of 400 to 600°C.

(9) A method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment as defined in another aspect of the present invention is the production method described in any of items (5) to (8), wherein the heat treatment is performed within a temperature range of 550 to 750°C.

(10) A method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment as defined in another aspect of the present invention is the production method described in any of items (5) to (9), wherein $(\text{Mg}, \text{Fe})\text{O}$ Wüstite containing Mg and Fe is formed in the grain boundary layer by heat treatment in the non-oxidizing atmosphere, and the grain boundary layer containing Wüstite is used as a filler containing either

silicon oxide at least containing iron oxide, or iron oxide at least containing Mg, by a heat treatment in the oxidizing atmosphere.

[0013]

(11) A method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment as defined in another aspect of the present invention is the production method described in any of items (5) to (10), wherein any of $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{SnO-P}_2\text{O}_3$, $\text{SiO}_2\text{-B}_2\text{O}_3\text{-ZnO}$, $\text{SiO}_2\text{-B}_2\text{O}_3\text{-R}_2\text{O}$ and $\text{Li}_2\text{O-ZnO}$ is used for the low melting glass.

(12) A method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment as claimed in another aspect of the present invention is the production method described in any of items (5) to (11), wherein any of Al_2O_3 , B_2O_3 , Sb_2O_3 and MoO_3 is used for the metal oxide.

Effects of the Invention

[0014] In the present invention, Fe-based soft-magnetic metal particles and an Mg-containing oxide coating film coating the surface of the soft-magnetic metal particles can be formed with tight adhesion. The Fe-based soft-magnetic iron particles with the Mg-containing oxide coating film are bonded on the surface side of the grain boundary layer containing a mixture of silicon resin, low melting glass or metal oxide component in the grain boundary layers thereof. Since iron oxide is dispersed and grown at the grain boundaries of joined portions, the surface side of the grain boundary layer and the Mg-containing oxide coating film can be adhered strongly. Because of the strong adhesion, a high-strength soft-magnetic composite compaction-heat treated material can be produced.

Moreover, since the Mg-containing oxide coating film can be placed around Fe-based soft-magnetic metal particles property, even after compaction molding, individual Fe-based soft-magnetic metal particles can be separated and insulated properly. Thus, high specific electrical resistance can be achieved in the entire soft-magnetic composite compaction-heat treated material, and a soft-magnetic composite compaction-heat treated material with suppressed eddy current loss can be produced.

In addition, since the surface layer portion where Fe-based soft-magnetic metal particles are joined on the surface side of the grain boundary layer has high strength, it contributes to strength of the entire soft-magnetic composite compaction-heat treated material.

[0015] The soft-magnetic composite material produced by compacting and heat treatment according to the present invention has high density, high strength, high specific electrical resistance and high magnetic flux density. The soft-magnetic composite material produced by compacting and heat treatment of the present invention is superior in terms of having the characteristics of high strength, high magnetic flux density and low high-frequency iron loss. Therefore, it can be used as a material of various types of electromagnetic circuit components by taking advantage of these characteristics.

In the soft-magnetic composite material produced by compacting and heat treatment of the present invention, the Mg-containing oxide film consists mainly of $(\text{Mg}, \text{Fe})\text{O}$, and as a low melting glass, any one of $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{SnO-P}_2\text{O}_3$, $\text{SiO}_2\text{-B}_2\text{O}_3\text{-ZnO}$, $\text{SiO}_2\text{-B}_2\text{O}_3\text{-R}_2\text{O}$ and $\text{Li}_2\text{O-ZnO}$ can be utilized. As a metal oxide, any one of Al_2O_3 , B_2O_3 , Sb_2O_3 or MoO_3 can be utilized. By having the composition described above, a soft-magnetic composite compaction-heat treated material having high density, high strength, high specific electrical resistance, and high magnetic flux density, can be practically produced.

[0016] According to the production method of the present invention, a soft-magnetic composite material that is produced by compacting and heat treatment, having the superior characteristics described above, can be produced. In the production method of the present invention in particular, a surface layer portion contributing to improved strength, can be formed by heat treatment in an oxidizing atmosphere. Because of the surface layer portion, a soft-magnetic composite compaction-heat treated material with high strength, high density, high specific electrical resistance and high magnetic flux density, can be produced.

A high-strength soft-magnetic composite material produced by compacting and heat treatment of the present invention can be used as, for example, a magnetic core, motor core, generator core, solenoid core, ignition core, reactor core, transformer core, choke coil core or magnetic sensor core of the electromagnetic circuit components. By using the high-strength soft-magnetic composite material, electromagnetic circuit components with superior performance can be provided in applications mentioned above.

Electrical equipment utilizing electromagnetic circuit components include motors, generators, solenoids, injectors, electromagnetic valve actuators, inverters, converters, transformers, relays and magnetic sensor systems. Because of the present invention, efficiency and performance of the electrical equipments can be improved, and additionally it can contribute to down-sizing and reducing weight of these equipments.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017]

5 FIG. 1A is a diagram showing the cross-sectional structure of a sample of a high-strength soft-magnetic composite material obtained by compacting and heat treatment as claimed in the present invention obtained in an example. FIG. 1B is a schematic diagram of an enlarged photograph showing a metal structure of a sample of a high-strength soft-magnetic composite material produced by compacting and heat treatment obtain in an example, in a cross-section view.

10 FIG. 2 is an enlarged photograph showing the metal structure of another example of a sample of a high-strength soft-magnetic composite material obtained by compacting and heat treatment as claimed in the present invention obtained in an example.

FIG. 3 is an X-ray diffraction diagram showing the results of elementary analysis at a position 111 on the sample shown in the photograph of FIG. 2.

15 FIG. 4 is an X-ray diffraction diagram showing the results of elementary analysis at a position 112 on the sample shown in the photograph of FIG. 2.

FIG. 5 is an X-ray diffraction diagram showing the results of elementary analysis at a position 113 on the sample shown in the photograph of FIG. 2.

FIG. 6 is an X-ray diffraction diagram showing the results of elementary analysis at a position 114 on the sample shown in the photograph of FIG. 2.

20 FIG. 7 is an X-ray diffraction diagram showing the results of elementary analysis at a position 115 on the sample shown in the photograph of FIG. 2.

FIG. 8 is an X-ray diffraction diagram showing the results of elementary analysis at a position 116 on the sample shown in the photograph of FIG. 2.

25 FIG. 9 is an enlarged photograph showing the metal structure of another example of a sample of a high-strength soft-magnetic composite material produced by compacting and heat treatment as claimed in the present invention obtained in an example.

FIG. 10 is an X-ray diffraction diagram showing the results of elementary analysis at a position indicated by the number "1" in the structure photograph shown in FIG. 9.

30 FIG. 11 is an X-ray diffraction diagram showing the results of elementary analysis at a position indicated by the number "2" in the structure photograph shown in FIG. 9.

FIG. 12 is an X-ray diffraction diagram showing the results of elementary analysis at a position indicated by the number "3" in the structure photograph shown in FIG. 9.

FIG. 13 is an X-ray diffraction diagram showing the results of elementary analysis at a position indicated by the number "4" in the structure photograph shown in FIG. 9.

35 FIG. 14 is an X-ray diffraction diagram showing the results of elementary analysis at a position indicated by the number "5" in the structure photograph shown in FIG. 9.

FIG. 15 is an X-ray diffraction diagram showing the results of elementary analysis at a position indicated by the number "6" in the structure photograph shown in FIG. 9.

40 FIG. 16 is an enlarged photograph showing the metal structure of another example of a sample of a high-strength soft-magnetic composite material produced by compacting and heat treatment as claimed in the present invention obtained in an example.

BRIEF DESCRIPTION OF THE REFERENCE SYMBOLS

[0018]

- 1. Fe-based soft-magnetic metal particles
- 2. Mg-containing oxide film
- 50 3. Mg-containing oxide-coated soft-magnetic particles
- 5. Surface side of a grain boundary layer
- 10. Soft-magnetic composite compaction-heat treated material
- 10a. Surface layer portion
- 10b. Inner layer portion

BEST MODE FOR CARRYING OUT THE INVENTION

[0019] The following provides an explanation of preferred embodiments of the present invention with reference to the

drawings.

In the present invention, first, Mg-containing oxide-coated soft-magnetic particles (powder), which is coated with an Mg-Fe-O ternary oxide deposition film containing (Mg, Fe)O on the soft-magnetic metal particles, are prepared.

The soft-magnetic metal particles can be prepared with the following raw material powders by any of the subsequently described methods from (A) to (D).

For the raw material powders to prepare Fe-based soft-magnetic metal particles, which is used in the method to produce Mg-containing oxide-coated soft-magnetic metal particles of the present invention, the conventionally and commonly known iron powder, the insulated iron powder, the Fe-Al iron-based soft-magnetic alloy powder, the Fe-Ni iron-based soft-magnetic alloy powder, the Fe-Si-Al iron-based soft-magnetic alloy powder, the Fe-Co iron-based soft-magnetic alloy powder, the Fe-Co-V iron-based soft-magnetic alloy powder or the Fe-P iron-based soft-magnetic alloy powder can be preferably used.

More specifically, the iron powder is preferably a pure iron powder. The insulated iron powder is preferably a phosphate-coated iron powder, or a silicon oxide- or aluminum oxide-coated iron powder prepared by drying and heat treatment, after addition of and mixing with a wet solution such as a silica sol gel solution (silicate) or alumina sol gel solution to coat the surface of the iron powder. The Fe-Al iron-based soft-magnetic alloy powder is preferably an Fe-Al iron-based alloy powder containing 0.1 to 20 % of Al, with residuals consisting Fe and inevitable impurities (for example, an alper powder having a composition consisting of Fe and 15% of Al).

[0020] The Fe-Ni iron-based soft-magnetic alloy powder is preferably a nickel-based soft-magnetic alloy powder containing 35 to 85 % of Ni, and further containing one or more than two elements from a group comprising, 5 % of Mo or less, 5 % of Cu or less, 2 % of Cr or less, and 0.5 % of Mn or less depending on necessity, with a residual consisting of Fe and inevitable impurities (for example, powder consisting of Fe and 49% Ni). The Fe-Cr iron-based soft-magnetic alloy powder is preferably an Fe-Cr iron-based soft-magnetic alloy powder containing 1 to 20 % of Cr, and further containing one or more than two elements from a group comprising of 5 % of Al or less and 5 % of Ni or less depending on necessity, with the residual consisting of Fe and inevitable impurities. The Fe-Si iron-based soft-magnetic alloy powder is preferably an Fe-Si iron-based soft-magnetic alloy powder containing 0.1 to 10 % of Si, with the residual consisting of Fe and inevitable impurities.

The Fe-Si-Al iron-based soft-magnetic alloy powder is preferably an Fe-Si-Al iron-based soft-magnetic alloy powder containing 0.1 to 10 % of Si and 0.1 to 20 % of Al, with the residual consisting of Fe and inevitable impurities. The Fe-Co-V iron-based soft-magnetic alloy powder is preferably an Fe-Co-V iron-based soft-magnetic alloy powder containing 0.1 to 52 % of Co and 0.1 to 3 % of V, with the residual consisting of Fe and inevitable impurities. The Fe-Co iron-based soft-magnetic alloy powder is preferably an Fe-Co iron-based soft-magnetic alloy powder containing 0.1 to 52 % of Co, with the residual consisting of Fe and inevitable impurities. The Fe-P iron-based soft-magnetic alloy powder is preferably an Fe-P iron-based soft-magnetic alloy powder containing 0.5 to 1.0 % of P, with the residual consisting of Fe and inevitable impurities (in the following descriptions, % refers to % by weight (wet%)).

[0021] An average diameter of the of the soft-magnetic metal particles is preferably within the range of 5 to 500 μm . One of the reasons for choosing this range is that if the average particle diameter is less than 5 μm , the compressibility of the powder decreases and the volume ratio of the soft-magnetic metal particles becomes low, thereby lowering the value of magnetic flux density, which is not desirable. Another reason is that if the average particle diameter exceeds 500 μm , eddy current within the soft-magnetic metal particles increases and magnetic permeability at high frequencies decreases.

[0022] Method (A): Using any of the above-mentioned soft-magnetic metal particles as a raw material powder, oxidation treatment is carried out by holding them at a temperature of 25 to 500°C in an oxidizing atmosphere. Then, Mg powder is added to and mixed with the raw material powder. The resulting mixed powder is heated in an inert gas atmosphere or vacuum atmosphere at a temperature of 150 to 1100°C and pressure of 1×10^{-12} to 1×10^{-1} MPa. If it is necessary, the material is further heated at a temperature of 50 to 400°C in an oxidizing atmosphere (room temperature refers to a temperature of 25°C in the following descriptions), and Mg-containing oxide-coated soft-magnetic metal particles (powder) with an oxide insulating film containing Mg on the surface of the soft-magnetic metal particles are produced. These Mg-containing oxide-coated soft-magnetic particles have considerably superior adhesiveness as compared with conventional Mg-containing oxide-coated soft-magnetic particles with a formed Mg ferrite film. Frequency of being damaged and exfoliation of the insulating coating on the Mg-containing oxide-coated soft-magnetic particles is kept low, even if a powder compact is produced by press forming. In addition, by heat treatment a powder compact of these Mg-containing oxide-coated soft-magnetic particles at a temperature of 400 to 1300°C, a soft-magnetic composite compaction-heat treated material obtains a structure in which an Mg-containing oxide film is uniformly dispersed at a grain boundary and is not concentrated at a grain boundary triple junction.

[0023] In the case of the production method described above, in which the mixed powder prepared by mixing the oxidation-treated soft-magnetic metal particles with Mg powders and heated in an inert gas atmosphere or vacuum atmosphere at a temperature of 150 to 1100°C and pressure of 1×10^{-12} to 1×10^{-1} MPa, it is preferable to heat the mixed powder under rallying motion.

[0024] Method (B): An oxide-coated soft-magnetic powder is prepared by leaving the above-mentioned soft-magnetic metal particles at a temperature of 25 to 500°C in an oxidizing atmosphere to form an oxide film on the surface of a soft-magnetic powder. After addition of a silicon monoxide powder, and after or during mixing of the silicon monoxide with the oxide-coated soft-magnetic powder, the mixed powder is heated at a temperature of 600 to 1200°C in a vacuum atmosphere. Then, after addition of an Mg powder, and after or during mixing of the Mg powder with the oxide-coated soft-magnetic powder, the resulting mixed powder is heated at a temperature of 400 to 800°C in a vacuum atmosphere. By the above-described method, an Mg-Si-containing oxide-coated soft-magnetic powder is prepared in which an Mg-Si-containing oxide film is formed on the surface of the soft-magnetic powder. A composite soft-magnetic sintered material produced with the Mg-Si-containing oxide-coated soft-magnetic powder prepared according to this method surpasses a conventional compound soft-magnetic sintered material produced by compression-molding and sintering a mixture including a compound forming SiO and powders of MgCO₃ or MgO, in terms of density, bending strength, specific electrical resistance and magnetic flux density.

[0025] Method (C): An oxide-coated soft-magnetic powder is prepared by leaving the above-mentioned soft-magnetic metal particles at a temperature of 25 to 500°C in an oxidizing atmosphere to form an oxide film of iron on the surface of a soft-magnetic powder. After addition of a silicon monoxide powder and Mg powder, and after or during mixing of the silicon monoxide and Mg powder with the oxide-coated soft-magnetic powder, the mixed powder is heated at a temperature of 400 to 1200°C in a vacuum atmosphere. By the above-described method, an Mg-Si-containing oxide-coated soft-magnetic powder is prepared in which an Mg-Si-containing oxide film is formed on the surface of the soft-magnetic powder. A composite soft-magnetic sintered material produced with the Mg-Si-containing oxide-coated soft-magnetic powder prepared according to this method surpasses a conventional compound soft-magnetic sintered material produced by compression-molding and sintering a mixture including a compound forming SiO and powders of MgCO₃ or MgO, in terms of density, bending strength, specific electrical resistance and magnetic flux density.

Method (D): An oxide-coated soft-magnetic powder is prepared by leaving the above-mentioned soft-magnetic metal particles at a temperature of 25 to 500°C in an oxidizing atmosphere to form an oxide film of iron on the surface of a soft-magnetic powder. After addition of an Mg powder, and after or during mixing of the Mg powder with the oxide-coated soft-magnetic powder, the mixed powder is heated at a temperature of 400 to 800°C in a vacuum atmosphere. By the above-described method, an Mg-containing oxide-coated soft-magnetic powder is prepared in which an Mg-containing oxide film is formed on the surface of the soft-magnetic powder.

After addition of a silicon monoxide powder, and after or during mixing of the silicon monoxide with the Mg-containing oxide-coated soft-magnetic powder, the mixed powder is heated at a temperature of 600 to 200°C in a vacuum atmosphere. By the above-described method, an Mg-Si-containing oxide-coated soft-magnetic powder is prepared in which an Mg-Si-containing oxide film is formed on the surface of the soft-magnetic powder. A composite soft-magnetic sintered material produced with the Mg-Si-containing oxide-coated soft-magnetic powder prepared according to this method surpasses a conventional compound soft-magnetic sintered material produced by compression-molding and sintering a mixture including a compound forming SiO and powders of MgCO₃ or MgO, in terms of density, bending strength, specific electrical resistance and magnetic flux density.

The amount of the silicon monoxide powder added is preferably within the range of 0.01 to 1% by weight, and the amount of the Mg powder added is preferably within the range of 0.05 to 1% by weight.

The vacuum atmosphere is preferably a vacuum atmosphere at a pressure of 1×10^{-12} to 1×10^{-1} MPa.

[0026] The silicon monoxide (SiO) powder used in the aforementioned production method is made of an oxide having the highest vapor pressure among silicon oxides. Thus, silicon oxide components are easily deposited on the surface of soft-magnetic metal particles by heating, and even if heated after mixing with silicon dioxide (SiO₂) having a low vapor pressure, a silicon oxide film with an adequate thickness might not be formed on the surface of the soft-magnetic metal particles. After addition of a silicon monoxide powder, and after or during mixing of the silicon monoxide with the oxide-coated soft-magnetic powder, the mixed powder is heated at a temperature of 600 to 1200°C in a vacuum atmosphere. By the above-described method, a silicon oxide film-coated soft-magnetic powder is prepared in which SiO_x (where, x is 1 or 2) film is formed on the surface of the soft-magnetic powder. Further, after addition of Mg powders to the silicon oxide film-coated soft-magnetic powders and during mixing of them, an Mg-Si-containing oxide-coated soft-magnetic powder coated by an Mg-Si-containing oxide film that is made of Mg-Si-Fe-O, can be prepared by heating in a vacuum atmosphere.

[0027] The oxide-coated soft-magnetic powder can be prepared by forming an iron oxide film on the surface of a soft-magnetic powder by leaving soft-magnetic metal particles at a temperature of 25 to 500°C in an oxidizing atmosphere (such as in air). Because of this iron oxide film, the particles can be coated with SiO and/or Mg more effectively. If the oxide-coated soft-magnetic powder is heated at a temperature higher than 500°C in an oxidizing atmosphere during production of the oxide-coated soft-magnetic powder, the soft-magnetic metal particles aggregate, resulting in the formation of soft-magnetic metal particle aggregates, and sintering. These prevent a uniform surface oxidation, and therefore are not desirable. Therefore, the heating temperature during production of the oxide-coated soft-magnetic powder is defined to be from room temperature to 500°C. A more preferable temperature range is from room temperature

to 300°C. The oxidizing atmosphere is more preferably a dry oxidizing atmosphere.

[0028] For the Mg-Si-containing oxide-coated soft-magnetic powder used in this invention, the amount of SiO powder added to the oxide-coated soft-magnetic powders is limited to 0.01 to 1% by weight. If the added amount of the SiO powder is less than 0.01% by weight, the thickness of the silicon oxide film formed on the surface of the oxide-coated soft-magnetic powder is inadequate, thereby causing an insufficient amount of Si to be contained in the Mg-Si-containing oxide film. It prevents having an Mg-Si-containing oxide film with high specific electrical resistance, and thereby making this undesirable. On the other hand, if the amount of SiO powder added exceeds 1% by weight, the thickness of SiO_x (where, x is 1 or 2) silicon oxide film formed is excessively thick. This might cause lower density of a soft-magnetic composite compaction-heat treated material, which is produced by compacting and heat treatment the prepared Mg-Si-containing oxide-coated soft-magnetic metal particles.

[0029] For the production method of an Mg-Si-containing oxide-coated soft-magnetic powder of this invention, the amount of Mg powder added is limited to 0.05 to 1% by weight. If the amount of Mg powder added is less than 0.05% by weight, the thickness of the Mg film formed on the surface of the oxide-coated soft-magnetic powder is inadequate, and consequently only an inadequate amount of Mg is incorporated in the Mg-Si-containing oxide film. Because of lack of adequate thickness of the Mg-Si-containing oxide film, having the amount of Mg powder less than 0.05 % is not desirable. On the other hand, if the amount of Mg powder added exceeds 1% by weight, the thickness of the formed Mg film becomes excessively thick, and the density of a soft-magnetic composite compaction-heat treated material obtained by compacting and heat treatment the resulting Mg-Si-containing oxide-coated soft-magnetic powder decreases, thereby making this undesirable.

[0030] In the production method of the Mg-Si-containing oxide-coated soft-magnetic powder used in this invention, adding and mixing SiO powder, Mg powder and a mixed powder of SiO powder and Mg powder to the oxide-coated soft-magnetic powder is carried out in a vacuum atmosphere at a temperature of 600 to 1200°C. Due to the low vapor pressure of SiO, even if a mixed powder is heated at a temperature below 600°C, a sufficiently thick SiO film or Mg-Si-containing oxide coating film cannot be obtained. On the other hand, if a mixed powder is mixed at a temperature above 1200°C, the soft-magnetic powder ends up sintering. Since it prevents having the intended Mg-Si-containing oxide-coated soft-magnetic powder, exposing the mixed powder at a temperature higher than 1200°C is not desirable. In addition, the heating atmosphere at that time is preferably a vacuum atmosphere at a pressure of 1×10^{-12} to 1×10^{-1} MPa. Moreover, heating the mixed powder in rolling motion is more preferable.

[0031] Soft-magnetic powder having an average particle diameter within the range of 5 to 500 μm is preferably used for the soft-magnetic metal particles used when preparing an oxide-coated soft-magnetic powder. The reason for this is that if the average particle diameter is less than 5 μm , the compressibility of the powder decreases and the volume ratio of the soft-magnetic powder becomes low, thereby causing reduction of the magnetic flux density value and making this undesirable. On the other hand, if the average particle diameter exceeds 500 μm , eddy current of the soft-magnetic powder increases, causing reduction of its magnetic permeability at high frequencies.

Oxidation treatment of the soft-magnetic metal particles makes them more susceptible to coating afterward. Oxidation treatment is carried out by leaving the particles at a temperature of 150 to 500°C in an oxidizing atmosphere or at a temperature of 50 to 100°C in distilled water or pure water. In either case, a temperature below 50°C is not efficient. On the other hand, if the temperature is held above 500°C in an oxidizing atmosphere, sintering occurs, thereby making this undesirable. The oxidizing atmosphere is preferably a dry oxidizing atmosphere.

[0032] Although the term "deposition film" normally refers to a film in which vacuum-deposited or sputtered atoms composing a film are deposited on, for example, a substrate, "a deposition film" as used in the present invention refers to a film in which iron oxide (Fe-O) and Mg of an Fe-based soft-magnetic powder with an iron oxide film are deposited on the surface of the Fe-based soft-magnetic metal particles accompanying reaction thereof. The film thickness of the Mg-Fe-O ternary oxide deposition film formed on the surface of the Fe-based soft-magnetic metal particles is preferably within the range of 5 to 500 nm in order to achieve high magnetic flux density and high specific electrical resistance of a soft-magnetic composite compaction-heat treated material after powder compaction. If the film thickness is less than 5 nm, the specific electrical resistance of the compacted soft-magnetic composite compaction-heat treated material is not adequate and eddy current loss increases, thereby making this undesirable. If the film thickness exceeds 500 nm, the magnetic flux density of the compacted soft-magnetic composite compaction-heat treated material decreases, thereby making this undesirable. The film thickness is more preferably within the range of 5 to 200 nm.

[0033] Mg-containing oxide-coated soft-magnetic particles produced according to the aforementioned method have an Mg-containing oxide film formed on the surface thereof. This Mg-containing oxide film reacts with silicon oxide or aluminum oxide to form a complex oxide and a complex oxide with high resistance interposes between grain boundaries of the soft-magnetic powder. As a consequence, a soft-magnetic composite compaction-heat treated material with high specific electrical resistance can be produced. In addition, a soft-magnetic composite compaction-heat treated material having superior mechanical strength can be produced, since sintered powders are mediated by the silicon oxide or aluminum oxide. In this case, coercivity can be held to low level since the main body of the sintered materials comprises silicon oxide or aluminum oxide. As a consequence, a soft-magnetic composite compaction-heat treated material having

low hysteresis loss can be produced. The aforementioned heat treatment is preferably carried out in an inert gas atmosphere or non-oxidizing atmosphere at a temperature of 400 to 1300°C. The words, "main body" refers to the component with the largest composite ratio in each composition. The words, "mainly consisted" and "mainly consisting", mean that the component has the largest composite ratio comparing with other compositions.

Production of Soft-Magnetic Composite Compaction-heat treated material

[0034] A soft-magnetic composite compaction-heat treated material is produced using Mg-containing oxide-coated soft-magnetic particles produced in the manner described above according to the previously explained methods. First, an insulating binder in the form of a silicone resin, low melting glass or metal oxide is mixed with the Mg-containing oxide-coated soft-magnetic particles, which is produced with the aforementioned methods, followed by compaction molding using an ordinary method and heat treatment in an inert gas atmosphere or non-oxidizing atmosphere to produce a precursor of a soft-magnetic composite compaction-heat treated material.

After the heat treatment process, the precursor is heat-treated at a temperature of 400 to 600°C in an oxidizing atmosphere such as a steam atmosphere or air, as subsequently described to produce an object of the present invention in the form of a soft-magnetic composite material obtained by compaction and heat treatment.

[0035] A defined amount of silicone resin or low melting glass including any of Bi_2O_3 - B_2O_3 , SnO - P_2O_3 , SiO_2 - B_2O_3 - ZnO , SiO_2 - B_2O_3 - R_2O and Li_2O - ZnO is incorporated in the Mg-containing oxide-coated soft-magnetic particles, which is produced according to the aforementioned methods.

The amount of silicone resin that is incorporated can be within the range of 0.2 to 1.5% by weight.

The amount of low melting glass that is incorporated can be within the range of 0.05 to 3.0% by weight.

Alternatively, a defined amount of metal oxide is incorporated in the Mg-containing oxide-coated soft-magnetic particles, instead of the silicone resin or low melting glass. Examples of the metal oxides include one or more than two metal oxides selected from the group consisting of aluminum oxide, boron oxide, vanadium oxide, bismuth oxide, antimony oxide and molybdenum oxide. These metal oxides are incorporated within the range of 0.05 to 1% by weight as Al_2O_3 , B_2O_3 , V_2O_5 , Bi_2O_3 , Sb_2O_3 and MoO_3 , and are compacted and molded after mixing. The resulting compact is then heat treated within a temperature range of 500 to 1000°C, and preferably 550 to 750°C, in a non-oxidizing atmosphere to produce a precursor of a soft-magnetic composite compaction-heat treated material, which is followed by heat-treating the precursor in an oxidizing atmosphere to produce a soft-magnetic composite material obtained by compaction and heat treatment. In addition, zinc stearate can also be used for the metal oxide.

Examples of atmospheres that can be selected for the heat treatment atmosphere include an inert gas atmosphere such as a nitrogen atmosphere, and a non-oxidizing atmosphere such as a hydrogen gas atmosphere.

[0036] In the present invention, heat treatment is carried out by heating within a temperature range of 400 to 600°C in an oxidizing atmosphere such as a steam atmosphere for the purpose of enhancing the bending strength or the like of the precursor of the soft-magnetic composite compaction-molded material.

As a result of carrying out this heat treatment in an oxidizing atmosphere, coated soft-magnetic particles (powder) in the precursor, in which an Mg-Fe-O ternary oxide deposition film containing (Mg, Fe)O is coated and formed on the surface of soft-magnetic particles, and an Mg-Fe-O ternary oxide deposition film containing (Mg, Fe)O present at the interface thereof, are transformed. The transformation results in a structure in which a plurality of Mg-containing oxide-coated soft-magnetic particles are bonded each other through the interposing the grain boundary layer and the intended soft-magnetic composite material obtained by compaction and heat treatment is produced at the end.

The Mg-containing oxide-coated soft-magnetic particles comprises soft-magnetic metal particles and the Mg-containing oxide coating on the surfaces of the soft-magnetic metal particles. The grain boundary layer comprises mainly of a silicon oxide containing an iron oxide (for example, a silicon oxide such as a silicone resin containing an iron oxide consisting mainly of Fe_3O_4 or FeO), an oxide containing a low melting glass component, or an iron oxide containing Mg.

[0037] Although a steam atmosphere at 400 to 600°C can be preferably selected for the aforementioned oxidizing atmosphere, heat treatment can be carried out in condition with heating within the aforementioned temperature range in an oxidizing atmosphere such as air.

If the temperature of the heat treatment conditions in the steam atmosphere is lower than 400°C, formation of Fe_3O_4 is not promoted, thereby possibly resulting in deterioration of strength. On the other hand, if temperature of the heating conditions exceeds 600°C, strength can be also deteriorated due to formation and decomposition of FeO ($4\text{FeO} \rightarrow \text{Fe}_3\text{O}_4 + \text{Fe}$).

[0038] As a reason why the iron oxide consisting mainly of Fe_3O_4 grows in the steam atmosphere by diffusing in the silicone resin, it is inferred that Fe diffuses through minute cracks, which are formed during molding, and crystal grains composing the MgO film. It is interpreted that strength is improved because the diffusing Fe is oxidized in the heat treatment in the oxidizing atmosphere and then the grain boundary layer is filled with the increasing iron oxide, which is mainly consisted of Fe_3O_4 , or in addition to Fe_3O_4 , iron oxides including FeO in part fill the grain boundary layer.

[0039] In the soft-magnetic composite material obtained by compaction and heat treatment obtained according to the

method explained above, connections between the Mg-containing oxide-coated soft-magnetic metal particles, which are comprised of the soft-magnetic metal particles and the Mg-containing oxide film coating the soft-magnetic metal particles, and the aforementioned low melting glass or the metal oxide, are the connections through the surface side grain boundary layers, and they are formed by mixing, compacting and heat-treating. The iron oxide present in the surface side grain boundary layer between the Mg-containing oxide-coated soft-magnetic particles is dispersed and grown as a result of the iron component thereof precipitating from the soft-magnetic metal particles at the grain boundary and forming an oxide. The Mg-containing oxide adjacent to the surface side grain boundary layer is obtained from an Mg-containing oxide film provided on the Mg-containing oxide-coated soft-magnetic particles prior to the aforementioned mixing, compacting and heat treatment.

The surface side grain boundary layer that surrounds the Mg-containing oxide-coated soft-magnetic particles has a structure mainly consisting of silicon oxide containing iron oxide (for example, a silicon oxide such as a silicone resin containing iron oxide consisting mainly of Fe_3O_4 or FeO), an oxide containing a low melting glass component, or an iron oxide containing Mg.

[0040] FIG. 1A shows the cross-sectional structure of an example of this type of soft-magnetic composite material obtained by compaction and heat treatment. This example of a soft-magnetic composite compaction-heat treated material 10 is in the shape of a disc, and has a bilayer structure in which a surface layer portion 10a having a thickness of 2 to 4 mm is formed on the surface layer side (in the case of a density of 7.5 g/cm^3) and an inner layer portion 10b formed to the inside thereof. The thickness of the surface layer portion 10a is affected by the density of the finished product of the soft-magnetic composite compaction-heat treated material. Although the thickness thereof is 2 to 4 mm in the case of a density of 7.5 g/cm^3 as described above, in the case of a density of 7.0 g/cm^3 , the thickness increases up to a maximum of about 15 mm, and becomes a thickness of about 0.3 mm depending on whether the density is increased and heat-treatment conditions. This is a result of a diffusion reaction of each element that occurs during heat treatment to be described later being affected by the steam atmosphere or other oxidizing atmosphere, and the effect in the direction of depth that the oxidizing atmosphere has on heat treatment is caused by the finished product of the soft-magnetic composite compaction-heat treated material having an effect on density.

FIG. 1B shows an enlarged view of a portion of the surface layer portions. 10a of the aforementioned example of a soft-magnetic composite compaction-heat treated material 10. In FIG. 1B, an Mg-containing oxide film 2 is formed so as to cover the surface of an Fe-based soft-magnetic particle 1 resulting in the formation of an Mg-containing oxide-coated soft-magnetic particle, and a soft-magnetic composite compaction-heat treated material includes a plurality of the Mg-containing oxide-coated soft-magnetic particles being bonded each other through an interposing surface side grain boundary layer 5.

Since the soft-magnetic composite compaction-heat treated material 10 is produced by compacting, heat treatment and heat-treating a plurality of Mg-containing oxide-coated soft-magnetic particles, the Mg-containing oxide-coated soft-magnetic particles preferably have an irregular shape and the Mg-containing oxide film 2 is formed over their entire surface. However, there is also the possibility of the presence of sites on the surface of the Mg-containing oxide-coated soft-magnetic particles where the Mg-containing oxide film 2 is only partially formed depending on the compaction and molding conditions. Each Mg-containing oxide-coated soft-magnetic particle is at least preferably covered with the Mg-containing oxide film so that overall specific electrical resistance of the soft-magnetic composite compaction-heat treated material does not decrease.

In this sense, even in the case in which the grain boundary layer 5 at the grain boundary triple junction where three soft-magnetic particles 1 have gathered is thicker than the grain boundary layer 5 at another site as shown in FIG. 1B, in the case there are differences in the thickness of the Mg-containing oxide film 2 at certain portions thereof, or in the case there are certain portions where coating is inadequate, such cases do not cause a problem as long as the overall specific electrical resistance of the soft-magnetic composite compaction-heat treated material as claimed in the present invention is high.

[0041] Although the duration of heat treatment in a steam atmosphere or in air for producing the soft-magnetic composite compaction-heat treated material 10 can be suitably adjusted within a range of several minutes to several hours, the effect of improving strength tends to be saturated if heat treatment is carried out beyond that which is necessary.

In the aforementioned structure in which a plurality of Mg-containing oxide-coated soft-magnetic particles are bonded each other through an interposing grain boundary layer consisting mainly of silicon oxide containing iron oxide (for example, a silicon oxide such as a silicone resin containing iron oxide consisting mainly of Fe_3O_4 or FeO), an oxide containing a low melting glass component, or an iron oxide containing Mg, is not formed throughout the entire thickness of the precursor. This structure is formed at the portion with a thickness of 2 to 4 mm from the uppermost surface of the precursor in the case of a density of 7.5 g/cm^3 under ordinary heat treatment conditions.

This is because the steam atmosphere or other oxidizing atmosphere does not have an effect on the formation of the grain boundary layer throughout the entire thickness of the precursor, but rather the effect is limited to a region having a certain thickness from the uppermost surface of the precursor. Namely, since a pathway for the oxidizing atmosphere is obstructed by the formation of oxide at the grain boundary, the oxidizing atmosphere is unable to be supplied to the

inside, thereby resulting in the formation of oxide occurring in a limited region from the surface.

For example, if a precursor having a thickness that exceeds the aforementioned thickness range is heat-treated in an oxidizing atmosphere, an inner layer portion is formed in which Fe-based Mg-coated soft-magnetic alloy powder is bound by the inside grain boundary layer formed as a result of being heat-treated in a state in which the central portion thereof

is either not affected or only slightly affected by the oxidizing atmosphere such as a steam atmosphere. In this inner layer portion, as a result of not being affected by the steam atmosphere or other oxidizing atmosphere, instead of a surface side grain boundary layer containing iron oxide consisting mainly of Fe_3O_4 or FeO , the Mg-containing oxide-coated magnetic particles are bonded by a grain boundary layer in which an Mg-Fe-O ternary oxide deposition film containing (Mg, Fe)O has been heat-treated, and an inner grain boundary layer including a grain boundary layer

consisting mainly of SiO_2 obtained by heat treatment a silicone resin. Since the Mg-containing oxide-coated soft-magnetic particles are bonded on the side of this inner layer portion by a grain boundary layer obtained by heat-treating an Mg-Fe-O ternary oxide deposition film and an inside grain boundary layer including the heat treated product of a silicone resin, instead of a surface side grain boundary layer formed as a result of being affected by a steam atmosphere or other oxidizing atmosphere, strength of the inside structure becomes deteriorated compared to that of the surface layer portion.

[0042] However, when a thickness of the surface layer portion 10, which demonstrates high strength, is about 2 to 4 mm from the uppermost surface of the surface layer portion of the precursor, in the case of a precursor density of 7.5 g/cm^3 , the soft-magnetic composite compaction-heat treated material 10, which is the final product, retain sufficiently high strength. In the surface layer portion 10a and the inner layer portion 10b, the periphery of the Mg-containing oxide-coated soft-magnetic particles is coated with a surface side grain boundary layer or inside grain boundary layer, which is formed based on an Mg-Fe-O ternary oxide deposition film. Therefore, an Mg-containing oxide coating, which is present around the soft-magnetic particles, magnetically isolates each soft-magnetic particle, and the soft-magnetic composite compaction-heat treated material, with high specific electrical resistance and low eddy current loss can be produced.

[0043] The soft-magnetic composite compaction-heat treated material 10 obtained according to the production method described above has high density, high strength, high specific electrical resistance and high magnetic flux density. Since this soft-magnetic composite compaction-heat treated material 10 has the characteristics of high magnetic flux density and low high-frequency iron loss, it can be used as a material of various types of electromagnetic circuit components by taking advantage of these characteristics.

In addition, the soft-magnetic composite compaction-heat treated material 10 obtained according to the production method described above is provided with a surface layer portion 10a in which soft-magnetic particles are bonded each other through an interposing surface side grain boundary layer containing a low melting glass component containing iron oxide consisting mainly of Fe_3O_4 , or a surface side grain boundary layer consisting mainly of a metal oxide containing iron oxide consisting mainly of Fe_3O_4 . These surface side grain boundary layers are grown by heat treatment an Mg-Fe-O ternary oxide deposition film containing (Mg, Fe)O and low melting glass or metal oxide present at the interface thereof in an oxidizing atmosphere. Therefore, each Mg-containing oxide-coated soft magnetic particle can be bonded properly, and even higher bending strength can be achieved. As a result, a soft-magnetic composite material with high strength can be obtained by compaction and heat treatment. Moreover, the soft-magnetic composite compaction-heat treated material produced according to the present production method has superior characteristics provided in addition to the characteristics of high magnetic flux density and low high-frequency iron loss.

[0044] Although the minimum value of the thickness of the surface layer portion 10a in the soft-magnetic composite compaction-heat treated material 10 cannot be uniformly defined since it is affected by the size and density of the finished product. In the case of a sample having a wall thickness of about 5 mm, a minimum thickness of 0.3 mm or more is preferable. In addition, in the case of a density of the finished product of 7.5 g/cm^3 , the thickness of the surface layer portion 10a is about 4 mm at a maximum even if temperature, duration and other parameters are controlled during heat treatment in an oxidizing atmosphere.

Example 1

[0045] Heat treatment was carried out on a soft-magnetic powder (pure iron powder) having an average particle diameter of 100 μm at 220°C in air for 0 to 60 minutes. The MgO film is proportional to the oxide film thickness formed during the heat treatment in air at 220°C of the previous stage. Thus, the amount of Mg added is only required to be the minimum required amount, 0.1% by weight of Mg powder was incorporated in the iron powder, and Mg-containing oxide-coated soft-magnetic particles were produced by rolling with a rolling granulation agitation mixer.

The results of measuring the thickness of the Mg-Fe-O ternary oxide deposition film containing (Mg, Fe)O formed on the outer periphery of the Mg-containing oxide-coated soft-magnetic particles (indicated with MgO film in Table 1) are shown in Table 1. Since the thickness of this film is proportional to the oxide film thickness formed by heat treatment in air as described above, samples having an MgO film thickness of 20 to 80 nm were used for the test samples.

[0046] Silicon resin was added to each of the MgO film thickness samples within the range of 0.3 to 1.5% as shown in Table 1, followed by heat treatment at the molding pressure and heat treatment conditions shown in Table 1. In addition, a sample was also prepared in which silicone resin was not added.

[0047]

[Table 1]

The sample no..	Iron powder avg. particle diameter (μm)	MgO mixing ratio	MgO film thickness (nm)	Amt. of Si resin added (wt%)	Molding pressure (t/cm^2)	Heat treatment conditions		
						Atmosphere	Temp. ($^{\circ}\text{C}$)	Time (min)
1	100 μm	0.1 wt%	40	0.3	9.3	N ₂	650	30
2					8	Air	650	30
3					8 (784 MPa)	Steam	560	75
4			20	0.4	9	N ₂	650	30
5			40					
6			80					
7				0*	9.3 (911 MPa)	N ₂	650	30
8				0.3				
9				0.7				
10				1				
11				1.5				
12			40	0.3	9 (882 MPa)	H ₂	650	30
13						Air*	650	30
14							550*	30
15							650	
16							750*	
17						N ₂	50	15
18								30
19								60
20								120
21								30
22								30
23								
24								30
25								
26								30
27				0.7	784 MPa	N ₂	650	

[0048] By heat treatment each sample under the heat treatment conditions shown in Table 1, a precursor of a soft-magnetic composite compaction-heat treated material was obtained comprised of an Mg-Fe-O ternary oxide deposition film containing (Mg, Fe)O and a silicone resin present at the interface thereof (and in the form of a plate measuring 60 mm $\times$ 10 mm $\times$ 5 mm). Then, heat treatment was carried out on the precursor under the temperature conditions shown

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in Table 2 in a steam atmosphere or in air, namely an oxidizing atmosphere, to obtain a target soft-magnetic composite material obtained by compaction and heat treatment.

[0049] Bending strength, specific electrical resistance, density, coercivity and magnetic flux density for each of the samples of the resulting soft-magnetic composite material obtained by compaction and heat treatment are shown in Table 2.

[0050]

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[Table 2]

Sample No.	Post-heat treatment conditions			Bending strength (MPa)	Specific electrical resistance ($\mu\Omega\text{m}$)	Density (g/cm^3)	Comercivity (A/m)	Magnetic flux density at 10000 (A/m) (T)	Surface layer thickness (mm)
	Atmosphere	Temp. ($^{\circ}\text{C}$)	Time (min)						
1	--	--	--	52*	1192	7.55	197	1.53	0
2	--	--	--	94*	1120	7.49	199	1.43	0.1
3	--	--	--	83*	1193	7.45	225	1.45	0.1

(continued)									
Sample No.	Post-heat treatment conditions			Bending strength (MPa)	Specific electrical resistance ($\mu\Omega\text{m}$)	Density (g/cm^3)	Comercivity (A/m)	Magnetic flux density at 10000 (A/m) (T)	Surface layer thickness (mm)
	Atmosphere	Temp. ($^{\circ}\text{C}$)	Time (min)						
4	Steam	560	150	182	492	7.52	217	1.46	4
5				178	549	7.50	215	1.41	4
6				153	613	7.46	228	1.26*	4
7		560	150	183	3*	7.56	198	1.42	4
8				204	261	7.54	214	1.43	4
9				188	1539	7.54	214	1.49	4
10				201	1548	7.50	216	1.48	4
11				194	1615	7.40	231	1.38	4
12		560	150	173	210	7.36	216	1.33	4
13			75	83*	972	7.49	205	1.45	0.1
14		560	75	74*	702	7.52	206	1.47	0.1
15				141	232	7.54	197	1.45	2.5
16				124	5*	7.55	196	1.49	2.5
17		60	75	155	188	7.56	205	1.45	2.5
18				141	232	7.54	197	1.45	2.5
19				160	214	7.55	207	1.45	2.5
20		560	150	183	187	7.55	194	1.50	4
21		560	225	200	222	7.54	209	1.44	4
22		400	150	106	319	7.53	218	1.53	0.3
23		450		126	435	7.55	241	1.50	0.3
24		500		118	338	7.53	245	1.49	0.3
25	Air	560	75	150	558	7.54	209	1.52	0.4
26			150	165	415	7.54	213	1.52	0.5

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(continued)

Sample No.	Post-heat treatment conditions			Bending strength (MPa)	Specific electrical resistance ($\mu\Omega\text{m}$)	Density (g/cm^3)	Comercivity (A/m)	Magnetic flux density at 10000 (A/m) (T)	Surface layer thickness (mm)
	Atmosphere	Temp. ($^{\circ}\text{C}$)	Time (min)						
27	Air	560	45	110	932	7.49	193	1.49	0.3

[0051] As shown in Table 2, bending strength of the sample nos. 1 to 3, which were not subjected to heat treatment after heat treatment, was within the range of 52 to 94 MPa. On the other hand, bending strength was improved in all cases for the sample nos. 4 to 12, 15, and 17 to 26, in which heat treatment was carried out at 400 to 560°C after having heat treated the samples at a temperature of 550 to 650°C in a non-oxidizing atmosphere such as a nitrogen gas atmosphere or hydrogen gas atmosphere.

However, in the sample no. 13, on which heat treatment was carried out in air, namely in an oxidizing atmosphere instead of a non-oxidizing atmosphere, bending strength was 83 and was not improved. In addition, in the sample no. 7, in which silicone resin was not added, specific electrical resistance was extremely low. Moreover, in the sample no. 16, in which heat treatment was carried out at 750°C, specific electrical resistance was also extremely low. In addition, in the sample no. 6, magnetic flux density decreased due to the thick film thickness of 80 nm.

On the basis of the above results, MgO film thickness is preferably within the range of 20 to 80 nm.

Based on the results above, it was found that more preferable heat treatment conditions are within the range of 400 to 560°C.

[0052] Next, based on the values of surface layer thickness shown in Table 2, it was found that the samples of soft-magnetic composite heat treated materials, demonstrating high strength have the surface side grain boundary layer in a portion 0.1 to 4 mm from the uppermost surface portion.

Although the thickness of the surface layer portion formed by heat treatment in air or heat treatment in a steam atmosphere is able to controlled somewhat according to the temperature and duration of heat treatment, the surface layer portion was formed at a thickness of 2 to 4 mm normally, even with modifications of conditions. In order to form the surface layer portion in regions at a depth beyond this range, it is necessary to significantly raise the heat treatment temperature or increase the duration of time for heat treatment, thereby making this disadvantageous in terms of productivity.

[0053] FIG 2 is an enlarged photograph showing the metal structure of the surface portion (a portion at a depth of 1 mm from the location of the uppermost surface) of the sample no. 8 of a high-strength soft-magnetic composite material obtained by compacting and heat treatment as claimed in the present invention obtained in the example.

Energy dispersive X-ray (EDX) analysis was carried out at positions 111, 112, 113, 114, 115 and 116 in the metal structure shown in FIG. 2. Those results are shown in FIGS. 3 to 8.

An analysis result for the position 111 of the soft-magnetic particles, is shown in FIG. 3. An analysis result for the position 112, which corresponds to a peripheral portion of the soft-magnetic particles, is shown in FIG. 4. An analysis result for the position 113, which corresponds to a portion predicted to be an Mg-containing oxide film located outside the soft-magnetic metal particles, is shown in FIG. 5. An analysis result for the position 114, which corresponds to the portion predicted to be an interface layer located outside the soft-magnetic metal particles, is shown in FIG. 6. An analysis result for the position 115, which corresponds to the portion predicted to be an Mg-containing oxide film located outside the soft-magnetic metal particles, is shown in FIG. 7. An analysis result for the position 116, which corresponds to a peripheral portion of the soft-magnetic metal particles, is shown in FIG. 8.

[0054] Based on the results shown in FIGS. 2 to 8, it was found that the peaks corresponding Fe were observed as the only major peak in analysis results for the soft-magnetic metal particles in FIGS. 3, 4 and 8. In contrast, large peaks corresponding to Mg and O were observed in addition to the peaks corresponding to Fe in the analysis results of sites predicted to be portions of the Mg-containing oxide film shown in FIGS. 5 and 7. Large peaks were observed for Mg and Si in addition to an Fe peak in the analysis results for a site predicted to be the grain boundary layer portion shown in FIG. 4. Therefore, it was confirmed that the metal structure of the surface portion (a portion at a depth of 1 mm from the location of the uppermost surface) of the sample no. 8 of the high-strength soft-magnetic composite material obtained by compaction and heat treatment, was formed as intended in the present invention.

[0055] FIG. 9 is an enlarged photograph of the metal structure of a surface portion (a portion at a depth of 0.5 mm from the location of the uppermost surface) of the sample no. 8 of the high-strength soft-magnetic composite material obtained by compaction and heat treatment as claimed in the present invention obtained in an example.

X-ray diffraction analyses were carried out at positions 1, 2, 3, 4, 5 and 6 in the metal structure shown in FIG. 9. These results are shown in FIGS. 10 to 15.

In FIG. 9, positions 1 and 2 correspond to the locations of the boundaries of three Mg-containing oxide-coated soft-magnetic particles in the form of grain boundary triple junctions. The position 3 corresponds to the location of another grain boundary triple junction. The positions 4 and 5 correspond to the boundaries of two Mg-containing oxide-coated soft-magnetic particles. The position 6 corresponds to a location near a boundary of three Mg-containing oxide-coated soft-magnetic particles in the form of a grain boundary triple junction.

[0056] Based on the results shown in each drawing, it was found that there are Fe, O and Mg in the boundary layer portions. Therefore it was confirmed that the metal structure of the surface portion (portion at a depth of 0.5 mm from the location of the uppermost surface) of the sample no. 8 of the high-strength soft-magnetic composite material obtained by compaction and heat treatment, is formed as intended in the present invention.

The Mn detected in FIGS. 14 and 15 is believed to be originated from an impurity in the iron powders. Since Mn has high affinity to oxygen, it could appear on the iron powder surface due to selective oxidization during oxidative heat treatment.

[0057] FIG. 16 is an enlarged photograph of the metal structure of the sample no. 8 of the high-strength soft-magnetic composite material obtained by compaction and heat treatment as claimed in the invention obtained in an example. As shown in FIG. 16, it was confirmed that there were the Mg-containing oxide films on the outer periphery of the soft-magnetic metal particles at a thickness of about 30 to 50 nm. In addition, it was confirmed that there was the surface side boundary layer of about the same width between the films.

[0058] While preferred embodiments of the present invention have been described and illustrated above, it should be understood that these are exemplary of the invention and are not to be considered as limiting. Additions, omissions, substitutions and other modifications of the composition of the present invention can be made without departing from the scope of the present invention. Accordingly, the present invention is not to be considered as being limited by the foregoing description, and is only limited by the scope of the appended claims.

INDUSTRIAL APPLICABILITY

[0059] The high-strength soft-magnetic composite material obtained by compaction and heat treatment (soft-magnetic material) according to the present invention can be used as an electromagnetic circuit component such as a magnetic core, motor core, generator core, solenoid core, ignition core, reactor core, transformer core, choke coil core or magnetic sensor core, and can be applied to an electromagnetic circuit component capable of demonstrating superior characteristics in any of these applications.

Examples of electrical equipment in which these electromagnetic circuit components are incorporated include motors, generators, solenoids, injectors, electromagnetic valve actuators, inverters, converters, transformers, relays and magnetic sensor systems, and in addition to enhancing the efficiency and performance of these electrical equipments, the size and weight thereof can be reduced.

Claims

1. A high-strength soft-magnetic composite material obtained by compaction and heat treatment, comprising a plurality of Mg-containing oxide-coated soft-magnetic particles bonded each other through an interposing grain boundary layer, wherein
the Mg-containing oxide-coated soft-magnetic particles are provided with Fe-based soft-magnetic particles and an Mg-containing oxide film coated on the surface of the soft-magnetic metal particles, and
the high-strength soft-magnetic composite material obtained by compaction and heat treatment is provided with a surface layer portion in which a plurality of the Mg-containing oxide-coated soft-magnetic particles are bonded each other through an interposing surface side grain boundary layer that mainly consists of at least one type of silicon oxide containing iron oxide consisting mainly of Fe_3O_4 or FeO and iron oxide containing Mg, and
an inner layer portion in which a plurality of the Mg-containing oxide-coated soft-magnetic particles are bonded each other through an interposing inside grain boundary layer that mainly consists of at least one type of silicon oxide and Mg-containing iron oxide.
2. A high-strength soft-magnetic composite material obtained by compaction and heat treatment according to claim 1, wherein bonds between the plurality of the Mg-containing oxide-coated soft-magnetic particles through the interposing grain boundary layer are formed by performing mixing, compacting and heat treatments in which the Mg-containing oxide-coated soft-magnetic particles, which comprise the soft-magnetic metal particles and the Mg-containing oxide film coated on the surface of the soft-magnetic particles are mixed with at least one selected from a group consisting of silicone resin, low melting glass and metal oxide, and the mixed materials are compacted and thereafter the compacted materials are heat treated,
the Fe_3O_4 or FeO in the surface side grain boundary layer between the Mg-containing oxide-coated soft-magnetic particles is dispersed and grown by precipitation of an Fe component from the Fe-based soft-magnetic metal particles at a grain boundary in the form of an oxide, and
the Mg-containing oxide film adjacent to the surface side grain boundary layer is obtained from an Mg-containing oxide coating film in the Mg-containing oxide-coated soft-magnetic particles before the mixing, compacting and heat treatments.
3. The high-strength soft-magnetic composite material obtained by compaction and heat treatment according to claim 2, wherein the Mg-containing oxide film includes mainly $(\text{Mg}, \text{Fe})\text{O}$, and the low melting glass includes any of $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{SnO-P}_2\text{O}_3$, $\text{SiO}_2\text{-B}_2\text{O}_3\text{-ZnO}$, $\text{SiO}_2\text{-B}_2\text{O}_3\text{-R}_2\text{O}$ and $\text{Li}_2\text{O-ZnO}$.
4. The high-strength soft-magnetic composite material obtained by compaction and heat treatment according to claim

2, wherein the Mg-containing oxide film includes mainly (Mg, Fe)O, and the metal oxide includes one or more than two metal oxides selected from a group consisting of Al_2O_3 , B_2O_3 , Sb_2O_3 and MoO_3 .

- 5 5. A method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment, comprising:

10 mixing an Mg-containing oxide-coated soft-magnetic particles, which are provided with Fe-based soft-magnetic metal particles and an Mg-containing oxide film coated on the surface of the soft-magnetic metal particles, with at least one selected from a group consisting of silicone resin, low melting glass, and metal oxide, compacting the mixed materials, and
15 heat treating the compacted materials in a non-oxidizing atmosphere to obtain a precursor of a soft-magnetic composite compaction-heat treated material, followed by heat-treating in an oxidizing atmosphere; wherein the heat treated material is provided with a surface layer portion on the surface of the precursor in which a plurality of the Mg-containing oxide-coated soft-magnetic particles are bonded each other through an interposing surface side grain boundary layer including a silicon oxide filler containing iron oxide at least consisting mainly of Fe_3O_4 or FeO , or an iron oxide filler at least containing Mg, and
20 the heat treated material is provided with an inner layer portion on the inside layer of the precursor in which a plurality of the Mg-containing oxide-coated soft-magnetic particles are bonded each other through an interposing inside grain boundary layer consisting of mainly at least one kind of iron oxide containing silicon oxide and iron oxide containing Mg.

- 25 6. The method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment according to claim 5, wherein the iron oxide in the grain boundary layer between the Mg-containing oxide-coated soft-magnetic particles of the surface layer portion is dispersed and grown by precipitation of an Fe component from the Fe-based soft-magnetic metal particles at a grain boundary in the form of an oxide.

- 30 7. The method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment according to claim 5, wherein the non-oxidizing atmosphere is an inert gas atmosphere, such as a nitrogen gas atmosphere, argon gas atmosphere, or a hydrogen gas atmosphere.

8. The method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment according to claim 5, wherein the oxidizing atmosphere is a steam or air atmosphere in a temperature range of 400 to 600°C.

- 35 9. The method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment according to claim 5, wherein the heat treatment is performed within a temperature range of 550 to 750°C.

- 40 10. The method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment according to claim 5, wherein (Mg, Fe)O Wüstite containing Mg and Fe is formed in the grain boundary layer by heat treatment in the non-oxidizing atmosphere, and the grain boundary layer containing Wüstite is used as a filler containing either silicon oxide at least containing iron oxide, or iron oxide at least containing Mg, by a heat treatment in the oxidizing atmosphere.

- 45 11. The method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment according to claim 5, wherein any of Bi_2O_3 - B_2O_3 , SnO - P_2O_3 , SiO_2 - B_2O_3 - ZnO , SiO_2 - B_2O_3 - R_2O and Li_2O - ZnO is used for the low melting glass.

- 50 12. A method for producing a high-strength soft-magnetic composite material obtained by compaction and heat treatment according to claim 5, wherein any of Al_2O_3 , B_2O_3 , Sb_2O_3 and MoO_3 is used for the metal oxide.

FIG. 1A

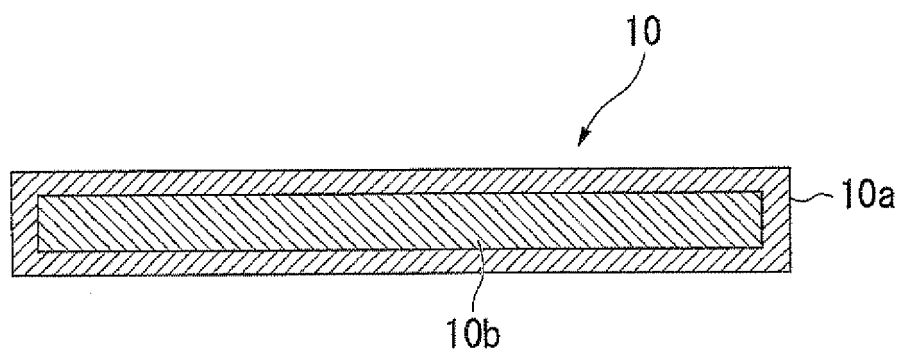


FIG. 1B

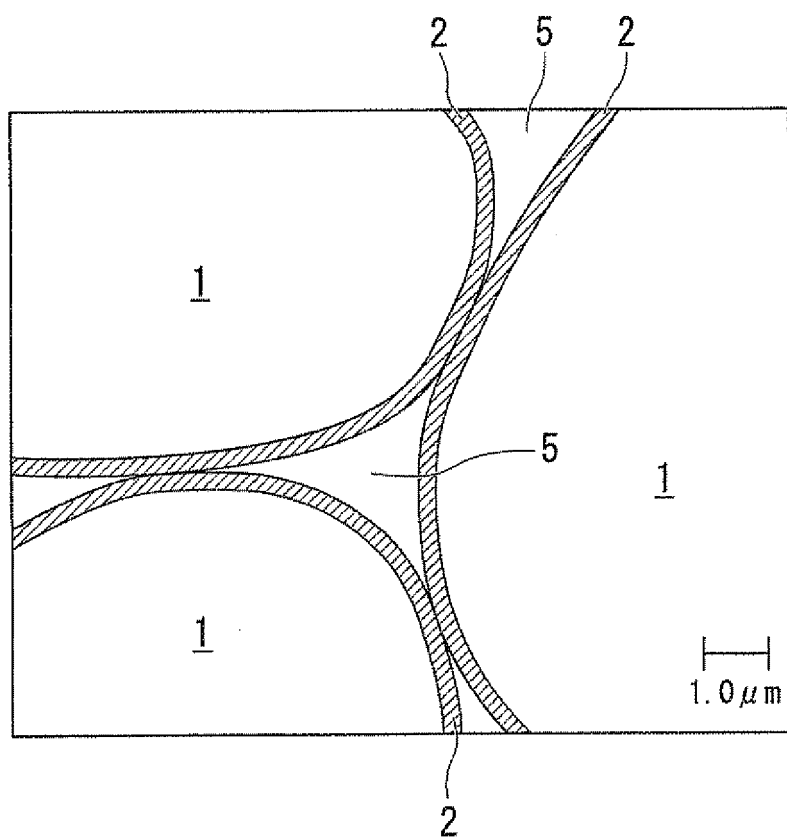


FIG. 2

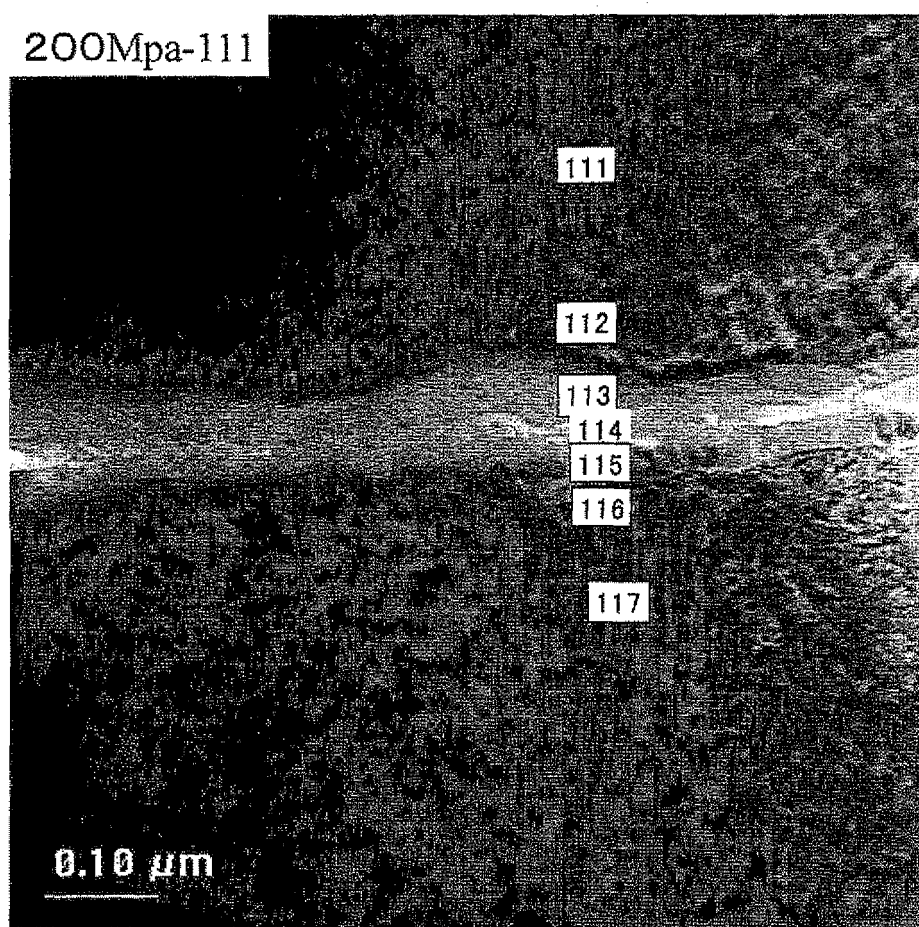


FIG. 3

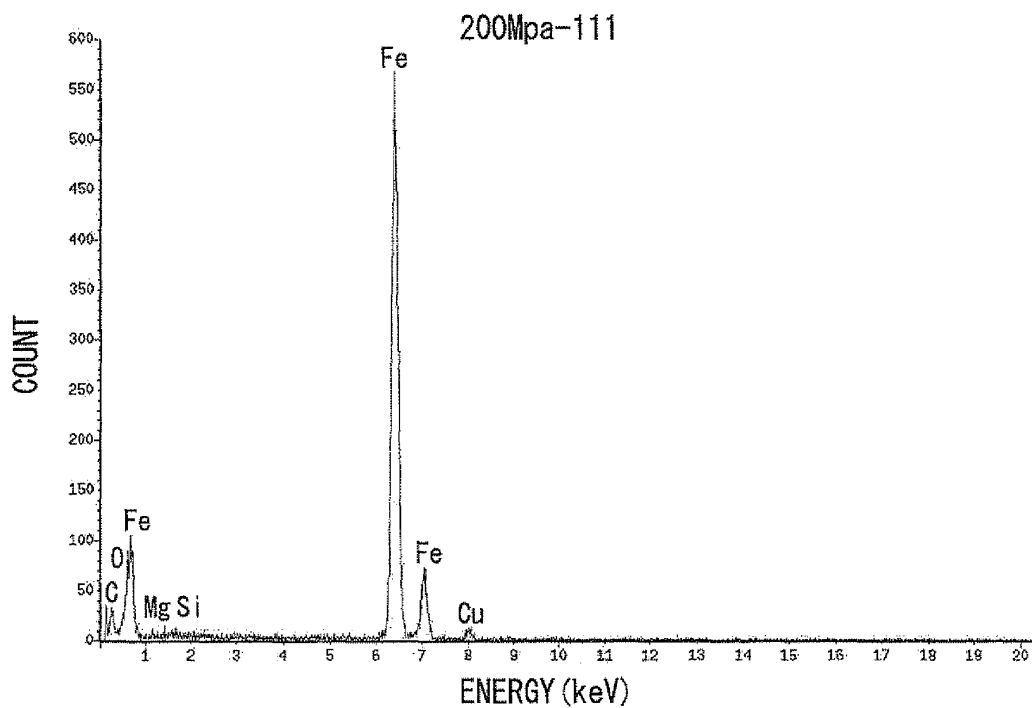


FIG. 4

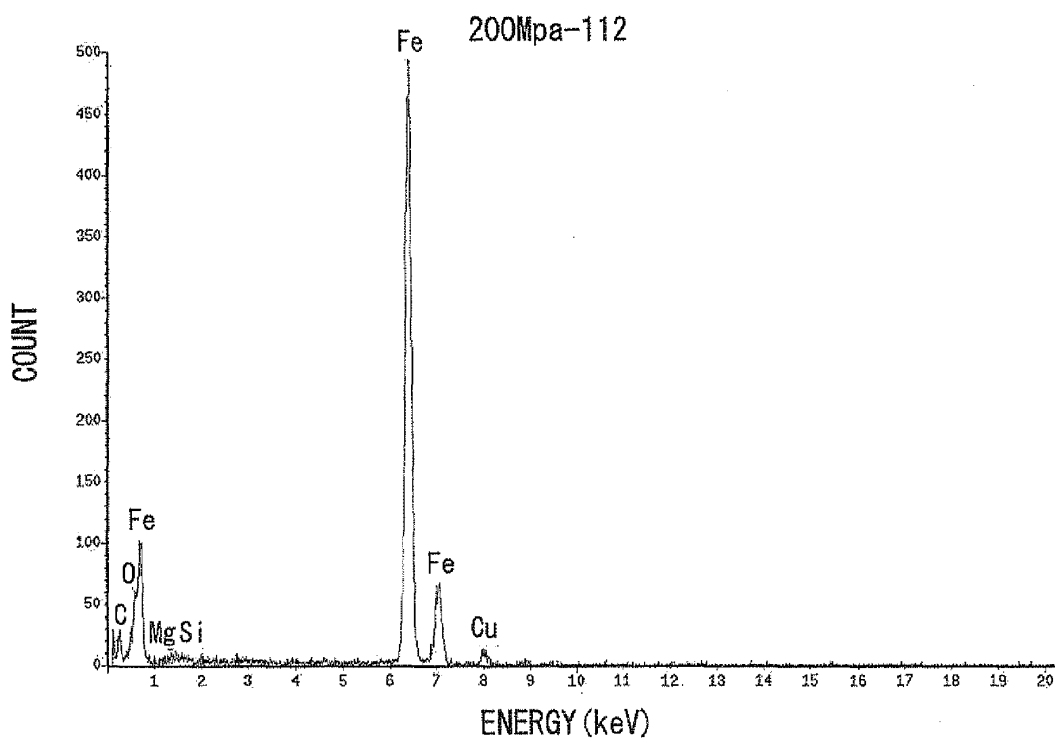


FIG. 5

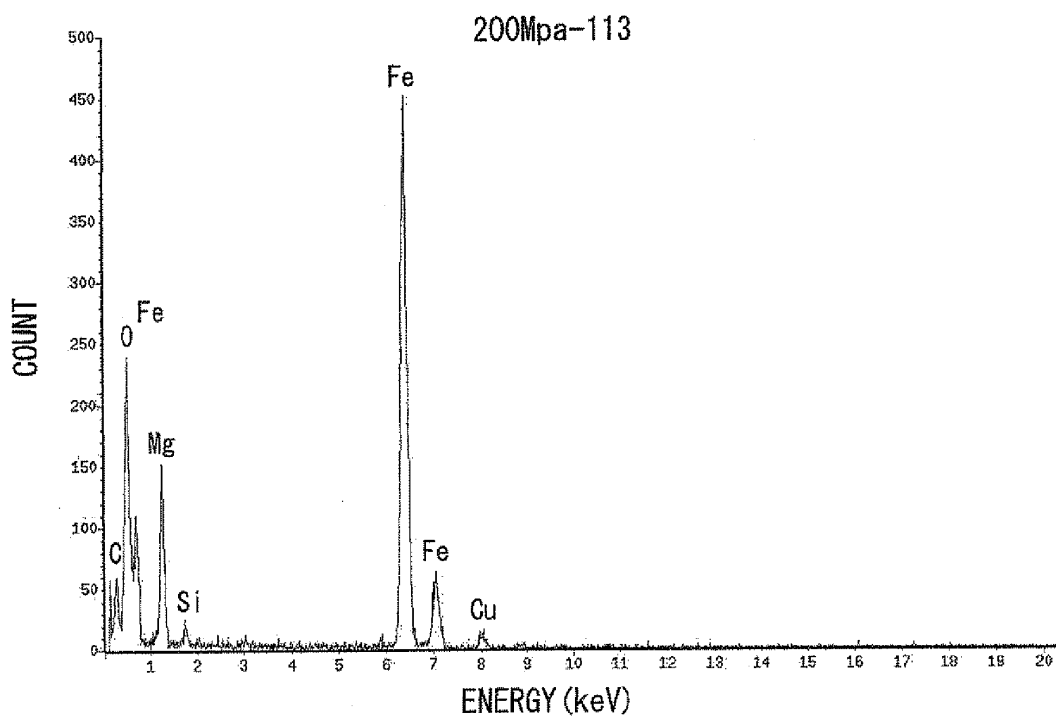


FIG. 6

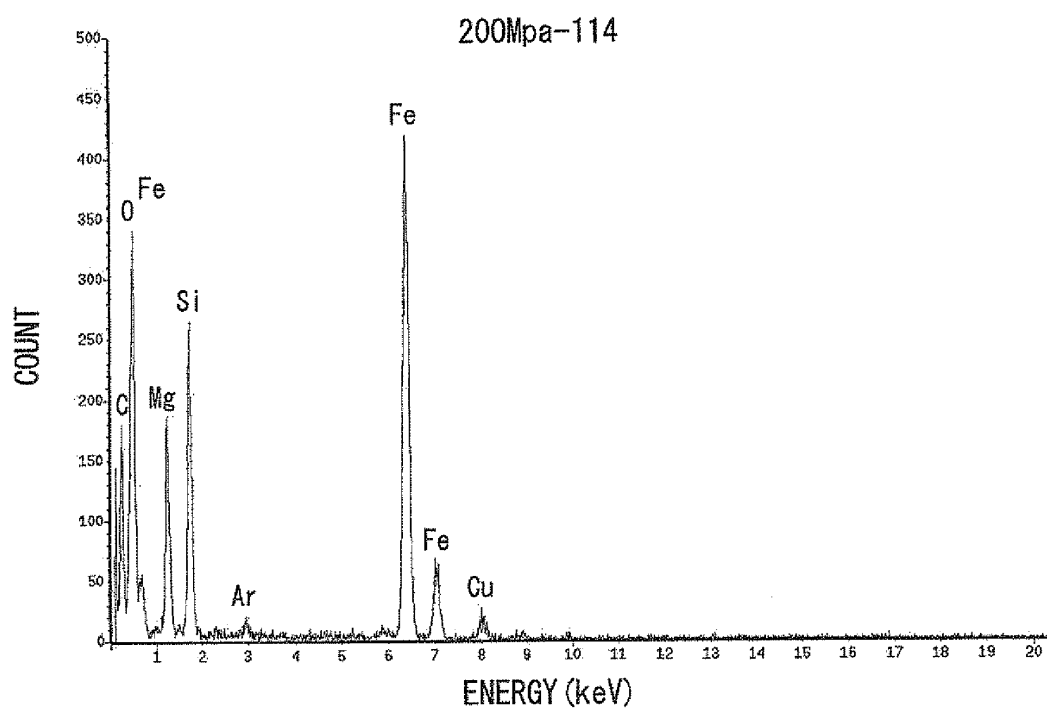


FIG. 7

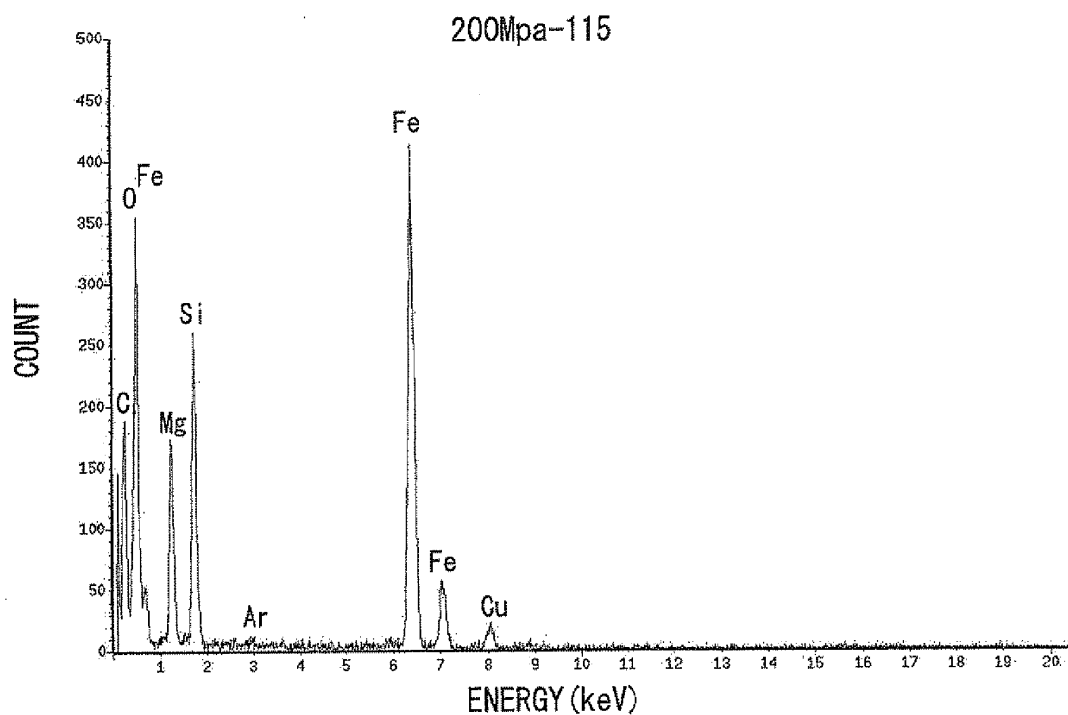


FIG. 8

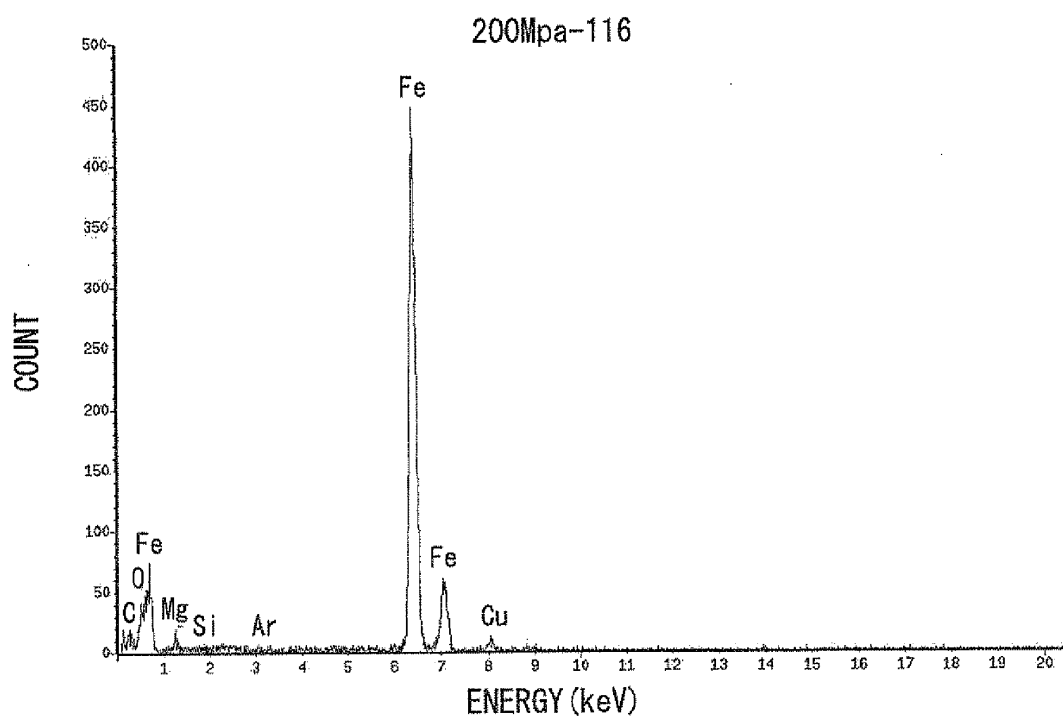


FIG. 9

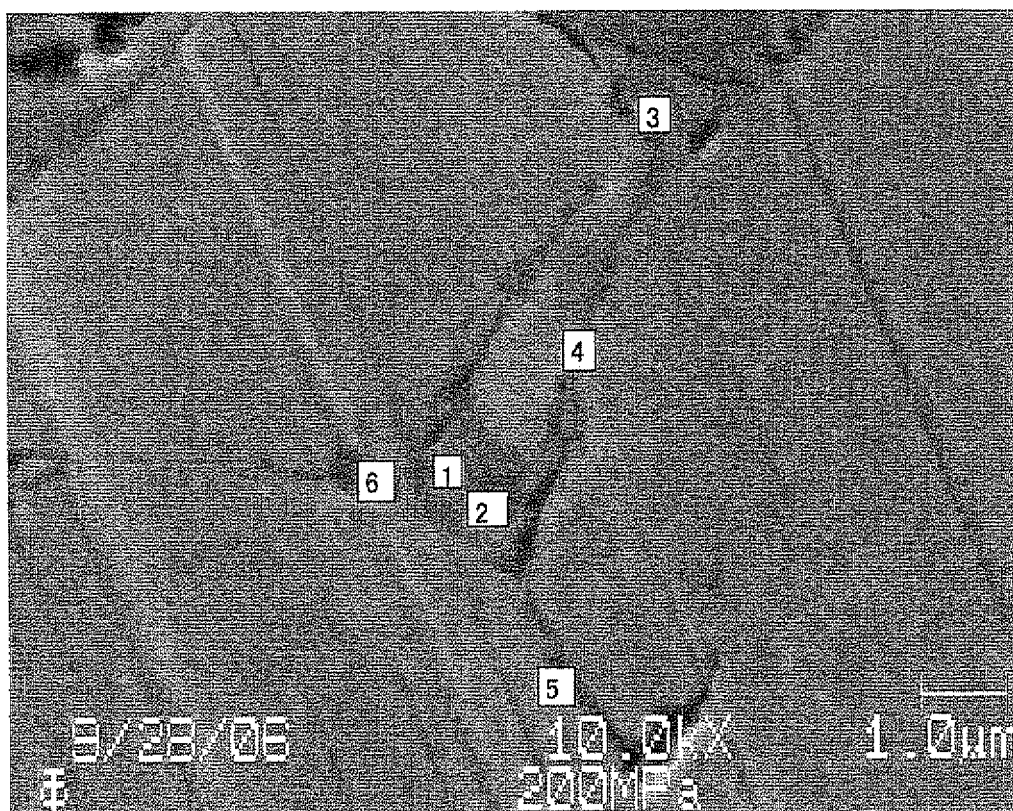


FIG. 10

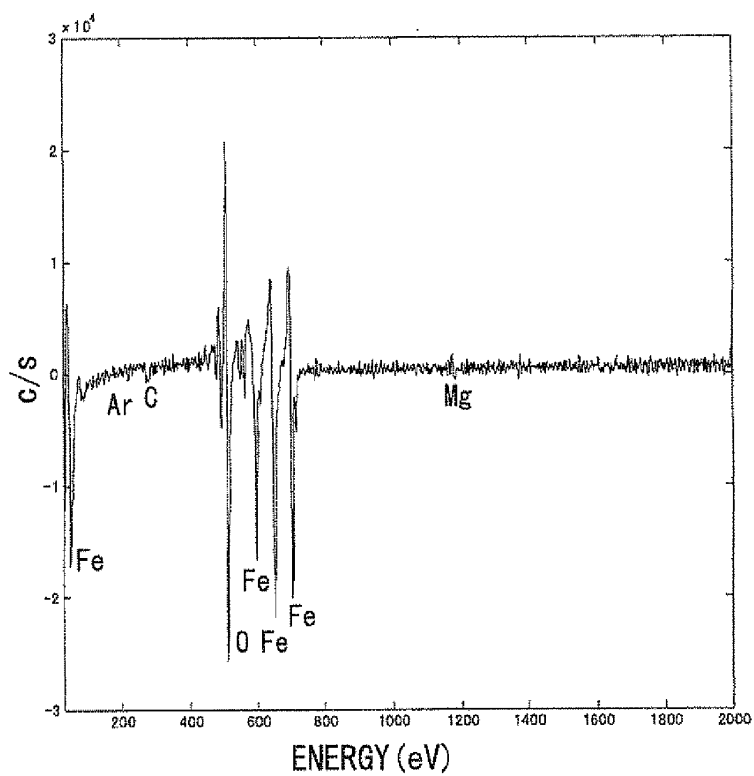


FIG. 11

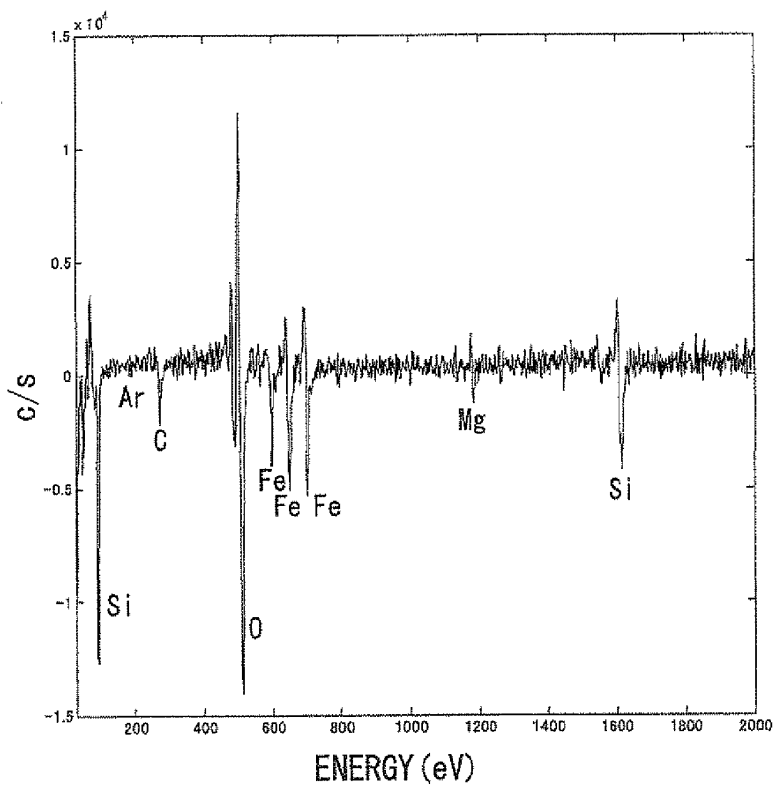


FIG. 12

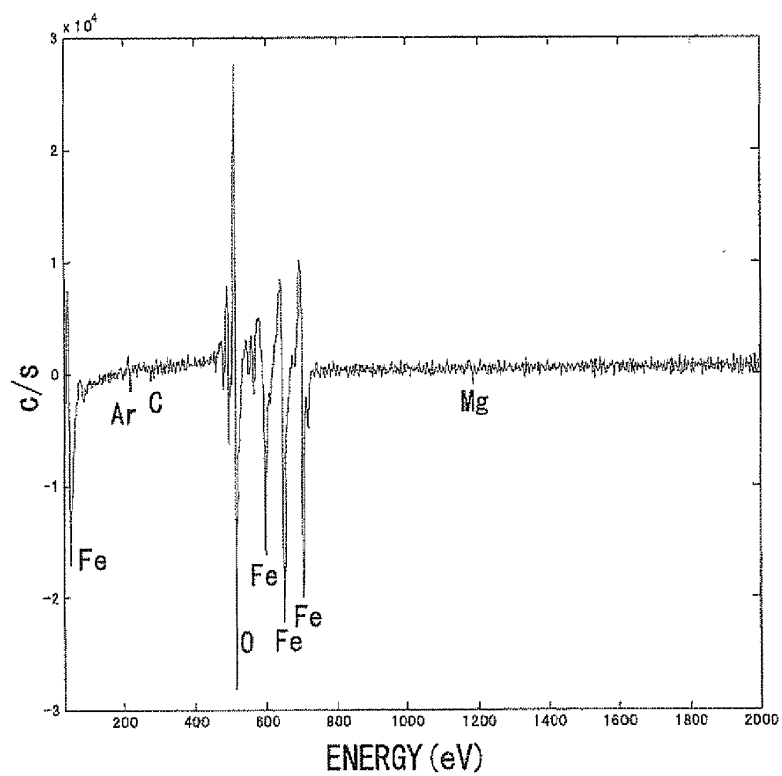


FIG. 13

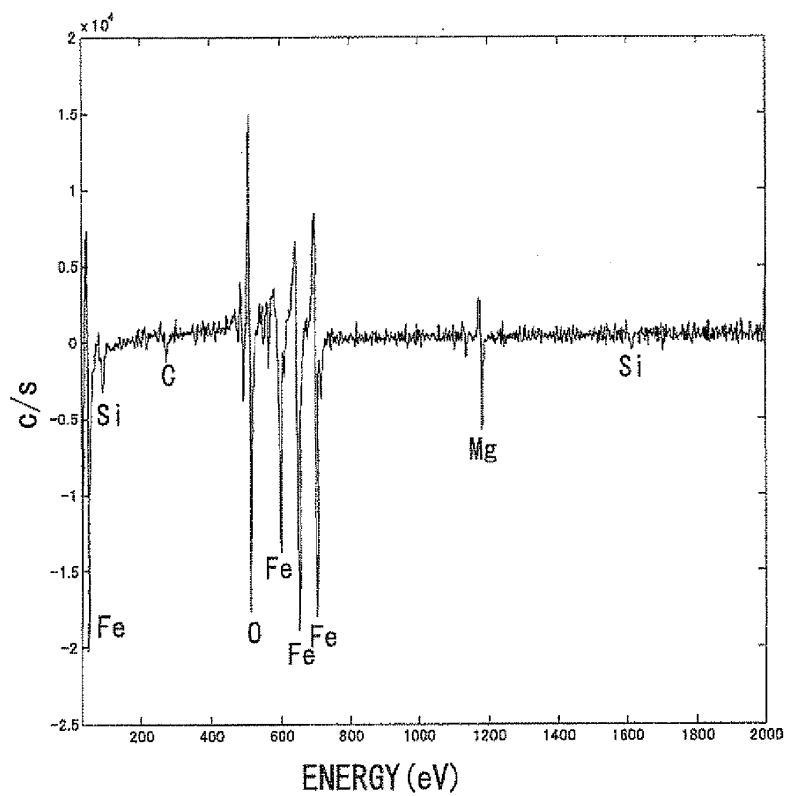


FIG. 14

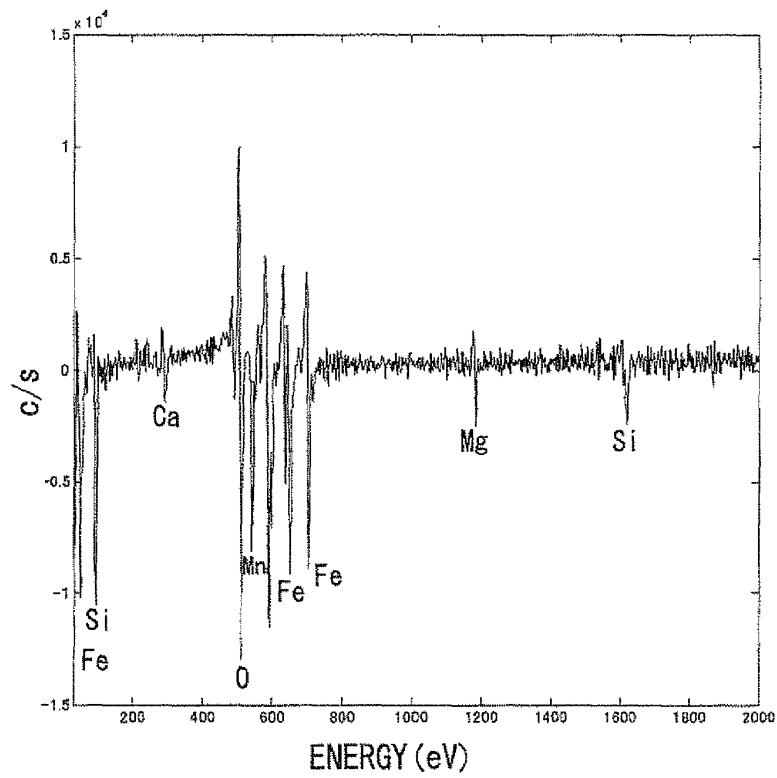


FIG. 15

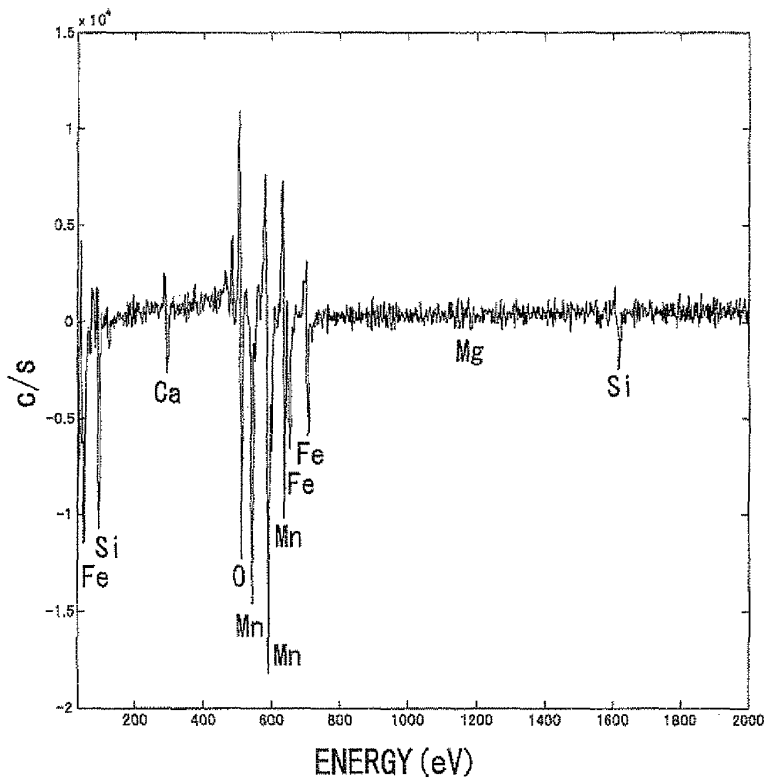
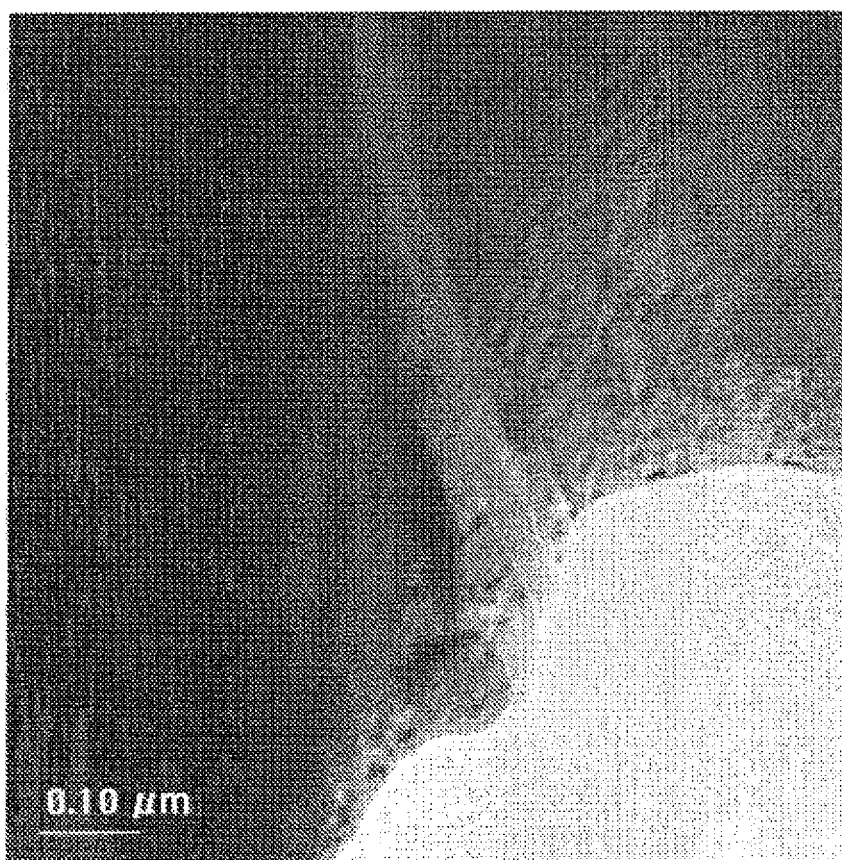


FIG. 16



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2008/070201

A. CLASSIFICATION OF SUBJECT MATTER

H01F1/33 (2006.01) i, B22F1/02 (2006.01) i, H01F1/24 (2006.01) i, H01F41/02 (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)

H01F1/33, B22F1/02, H01F1/24, H01F41/02

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	1996-2008
Kokai Jitsuyo Shinan Koho	1971-2008	Toroku Jitsuyo Shinan Koho	1994-2008

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.
Y	WO 2007/052772 A1 (Mitsubishi Materials PMG Corp.), 10 May, 2007 (10.05.07), Par. Nos. [0006], [0007], [0015] & JP 2007-070719 A & US 2008/0003126 A1 & EP 1808242 A1 & CA 2578861 A	1-12
Y	JP 9-74011 A (TDK Corp.), 18 March, 1997 (18.03.97), Claims 1, 5 to 7 (Family: none)	1-12
Y	JP 2006-332525 A (Mitsubishi Materials PMG Corp.), 07 December, 2006 (07.12.06), Par. Nos. [0015], [0024], [0025] (Family: none)	3, 11

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

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"&" document member of the same patent family

Date of the actual completion of the international search
26 November, 2008 (26.11.08)Date of mailing of the international search report
09 December, 2008 (09.12.08)Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2008/070201

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2007-162103 A (Hitachi Metals, Ltd.), 28 June, 2007 (28.06.07), Claim 1; Par. No. [0010] (Family: none)	4, 12
P, X	JP 2008-244347 A (Mitsubishi Materials PMG Corp.), 09 October, 2008 (09.10.08), Full text; all drawings (Family: none)	1-12
A	JP 2005-243794 A (Matsushita Electric Industrial Co., Ltd.), 08 September, 2005 (08.09.05), Par. No. [0039] (Family: none)	7, 8
A	JP 2005-113169 A (Matsushita Electric Industrial Co., Ltd.), 28 April, 2005 (28.04.05), Par. Nos. [0044] to [0046] & US 2005/0072955 A1 & EP 1521276 A2 & CN 1637962 A	7, 8
A	JP 2006-185981 A (Mitsubishi Materials PMG Corp.), 13 July, 2006 (13.07.06), Claim 3 (Family: none)	5

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2007289774 A [0001]
- JP H5258934 B [0004]
- JP S63158810 B [0004]
- JP 2004253787 A [0004]
- JP 2004297036 A [0004]