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(54) **CORROSION-RESISTANT SINTERED NEODYMIUM-IRON-BORON MAGNET RICH IN
LANTHANUM AND CERIUM, AND MANUFACTURING METHOD**

(57) The present invention discloses a corrosion-resistant sintered NdFeB magnet and a manufacturing method. The method comprises the following operation steps: preparing a NdFeB rare earth permanent magnet material alloy; preparing an alloy material rich in Co; breaking the NdFeB rare earth permanent magnet material alloy; uniformly mixing the prepared alloy material rich in Co into NdFeB rare earth permanent magnet material alloy powder according to a certain mass percentage; pressing and molding the mixed alloy powder into a blank in an oriented magnetic field $\geq 1.5T$ under the

protection of a nitrogen atmosphere; placing the molded blank in a high-vacuum sintering furnace for high-temperature sintering, and performing a two-stage tempering process to obtain the corrosion-resistant sintered NdFeB magnet. The present invention has the beneficial effects that more Co elements in the magnet are distributed on a grain boundary of the magnet through the innovation of the manufacturing method, and the corrosion resistance of the magnet is improved on the basis of ensuring the magnetic property of the magnet.

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Description**Technical Field**

[0001] The present application relates to the technical field of neodymium-iron-boron (NdFeB) magnets rich in lanthanum and/or cerium, and more particularly relates to a corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium and a manufacturing method.

Background Art

[0002] An NdFeB-based rare earth permanent magnet material is a third-generation rare earth permanent magnet functional material invented in the early 1980s, which has excellent magnetic properties of high remanence, high coercivity and high magnetic energy product, is thus widely used in automation technology, communication and transportation technology, information technology, aerospace technology and other sectors of the national economy, and becomes one of important basic materials supporting the contemporary electronic information industry. By this year, the usage has reached 100,000 tons, and the material has become an important material basis of modern science and technology and people's livelihood.

[0003] With the improvement of material usage, the amount of rare earth materials used as a main raw material for material manufacturing is continuously increasing. More importantly, the application field of rare earth materials as "vitamins" of modern industry is not limited to the production of rare earth permanent magnet materials. For example, in recent years, manufacturers of sintered NdFeB permanent magnet materials use relatively low-priced rare earth gadolinium element to partially replace more expensive rare earth praseodymium and neodymium elements to produce low-cost sintered NdFeB magnets, but the important application field of gadolinium is in the field of magnetic refrigeration materials and optical information storage sectors, so it is a waste of manufacturing low-cost sintered NdFeB permanent magnets with gadolinium instead of neodymium in a strict sense. Once gadolinium is found to have more important application, irreparable loss will be caused. Partial replacement of neodymium with holmium also has the same result and problem.

[0004] In the prior art, the two rare earth elements Pr and Nd are the main raw materials for producing sintered NdFeB rare earth permanent magnet materials, and the average use amount in materials is about 19 wt% to 33 wt%. However, in order to obtain some high-coercivity magnet materials, a small amount of Dy and Tb heavy rare earth elements and other non-rare earth metals such as Nb, Cu, Al, Ga, Ti, V, Mn, Zn, Zr, W, Si, Sn, Cr and Mo also need to be properly added to compose the ratio of the entire material. In the current domestic manufacturing level of sintered NdFeB permanent magnet materials, the mass production of medium and low grade products with Hcj less than or equal to 17kOe no longer needs to add Dy, Tb and other heavy rare earth elements, but the dependence on Pr and Nd as two kinds of light rare earth elements is increasingly prominent. The two elements Pr and Nd only account for 6 to 7wt% content in rare earth minerals. In order to meet the production of sintered NdFeB permanent magnet materials rich in lanthanum and/or cerium, the exploitation of rare earth resources is bound to be accelerated, causing the generation of more high-peak rare earth waste ore rich in lanthanum and/or cerium, thus increasing environmental pollution.

[0005] Therefore, if lanthanum cerium rare earth elements can be used to partially replace praseodymium neodymium materials for manufacturing NdFeB rare earth permanent magnet materials, the cost of materials can be reduced and a balanced use effect of resources can be achieved. However, due to easier oxidation of lanthanum and cerium elements than praseodymium and neodymium, the sintered NdFeB permanent magnet material with added lanthanum and cerium elements has worse corrosion resistance. Even if plated with some metal coating and placed in the air, a magnet will be severely corroded half a year later, with almost no practical value.

[0006] Based on these reasons, the improvement of the corrosion resistance of sintered NdFeB materials rich in lanthanum and/or cerium per se has become the basis of the material having practical value. The main reason for the corrosion of an NdFeB magnet lies in the electrode potential difference between a main phase and a phase rich in neodymium, in which the electrode potential of the main phase is higher than the electrode potential of the phase rich in neodymium, so that the phase rich in neodymium becomes an anode in the "galvanic reaction" to accelerate the corrosion of the phase rich in neodymium, resulting in continuous intergranular corrosion of crystal grains in the magnet. The main phase is exfoliated and pulverized due to the loss of a grain boundary phase, so as to complete the macroscopic oxidation of the permanent magnet. Therefore, how to reduce the potential difference between two phases in a sintered NdFeB magnet is the key to improve the corrosion resistance of the magnet.

[0007] In order to counteract this mechanism, people add elements Co and Cu to a material to increase the corrosion resistance of sintered Nd-Fe-B materials, wherein element Cu is added as a small metal in an amount that is not excessive (0.05 wt% to 0.25 wt%), and element Cu forms a mass phase at a grain boundary of the magnet, and generally does not participate in the replacement of a main phase element, so an effect on the magnetic property is little. However, Co element will be distributed in the grain boundary of the magnet, and can replace Fe element to form an Nd₂Co₁₄B phase,

thereby reducing the magnetic property of the material.

Summary of the Invention

[0008] In order to overcome the above defects in the prior art, the present invention provides a corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium and a manufacturing method, which can improve the corrosion resistance of the magnet based on ensuring the magnetic property of the magnet.

[0009] In order to achieve the above object, the present invention adopts the following technical schemes:

A corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium comprises an NdFeB rare earth permanent magnet material rich in lanthanum and/or cerium and an alloy material rich in Co for improving corrosion resistance of the material, wherein components of the NdFeB rare earth permanent magnetic material rich in lanthanum and/or cerium are $\text{Re}_\alpha\text{Fe}_{100-\alpha-\beta-\gamma}\text{B}_\beta\text{M}_\gamma$, in which Re is a rare earth element, including two or more than two elements selected from La, Ce and Nd, and inevitably containing Nd element; M is an additive element, including one or more than one element selected from Ti, V, Cr, Ni, Zn, Ga, Ge, Al, Zr, Nb, Co, Cu, Ag, Sn, W, Pb, Bi and Pd; Fe is Fe and unavoidable impurities; α , β and γ are the atomic percentage contents of the elements, wherein $12 \leq \alpha \leq 17$, $5.1 \leq \beta \leq 6.8$, and $0.1 \leq \gamma \leq 7.8$; the alloy material rich in Co includes two or more than two elements selected from Pr, Nd, Gd, Ho, Co, Ti, V, Zn, Ga, Al, Zr, Nb, Cu, Ag, Sn, Pb and Pd, and inevitably contains Co.

[0010] The present invention applies an alloy material rich in cobalt for improving the corrosion resistance of a material to doping and modifying an NdFeB rare earth permanent magnet material rich in lanthanum and/or cerium, so that more Co element in the sintered NdFeB magnet can be distributed on a grain boundary instead of forming an $\text{Nd}_2\text{Co}_{14}\text{B}$ phase that affects the magnetic property of the magnet, which is conducive to the preservation of the magnetic property of the material and the improvement of the corrosion resistance of the grain boundary of the magnet.

[0011] Preferably, La and Ce elements in the rare-earth element Re account for 15 wt% to 45 wt% of the total use amounts of rare earth in the NdFeB rare earth permanent magnet material rich in lanthanum and/or cerium. The use of lanthanum and cerium light rare earth elements instead of praseodymium and neodymium rare earth elements will slow down the exploitation of rare earth resources and reduce the generation of high-peak rare earth waste ore rich in lanthanum and/or cerium, so as to reduce environmental pollution.

[0012] Preferably, the rare earth element Re further comprises one or more than one element selected from Pr, Pm, Sm, Eu, Gd, Ho, Er, Tm, Yb, Lu, Y and Sc.

[0013] Preferably, the alloy material rich in Co inevitably does not contain element Fe to improve the corrosion resistance of the grain boundary of the magnet.

[0014] The present invention also provides a manufacturing method of a corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium, which comprises the following specific operation steps:

- (1) Preparing an NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium according to components of an NdFeB rare earth permanent magnet material rich in lanthanum and/or cerium;
- (2) Preparing an alloy material rich in Co according to components of the alloy material rich in Co;
- (3) Breaking the NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium to obtain NdFeB rare earth permanent magnet material alloy powder rich in lanthanum and/or cerium with an average particle size of 2.5 to 4.5 μm ;
- (4) Adding the alloy material rich in Co obtained in step (2) into the NdFeB rare earth permanent magnet material alloy powder rich in lanthanum and/or cerium according to a certain mass percentage content, wherein a process of pulverizing and mixing the alloy material rich in Co makes the alloy material rich in Co to be uniformly mixed into the NdFeB rare earth permanent magnet alloy powder rich in lanthanum and/or cerium;
- (5) Pressing and molding the mixed alloy powder into a blank in an oriented magnetic field $\geq 1.5\text{T}$ under the protection of a nitrogen atmosphere;
- (6) Placing the molded blank in a high-vacuum sintering furnace for high-temperature sintering, and performing a two-stage tempering process to obtain the corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium.

[0015] After the above process, the prepared corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium will be composed of a phase rich in Nd, a main phase ($\text{Nd}_2\text{Fe}_{14}\text{B}$), alloy powder rich in Co and a very small amount of phase rich in B ($\text{Nd}_{1.1}\text{Fe}_4\text{B}_4$). The alloy powder rich in Co exists between gaps of main phase particles.

[0016] Preferably, a preparation process adopted in step (1) and step (2) is a casting process or a quick-setting sheet process; and in step (3), a breaking method adopted is mechanical breaking or hydrogen breaking plus jet milling.

[0017] Preferably, the preparation process adopted in step (1) and step (2) is a quick-setting sheet process.

[0018] Preferably, a roller speed of a cooling copper roller used in the quick-setting sheet process of step (2) is 5 to 15 times of a roller speed of a cooling copper roller used in the quick-setting sheet process of step (1), wherein 5 to 15

times of the roll speed is a preferred solution, and in step (2) preparation can also be performed at the same roll speed as that in step (1).

[0019] Preferably, in step (4), the mass percentage content of the alloy material rich in Co in the NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium is 1% to 5%.

[0020] Preferably, in step (6), sintering temperature is 1030 °C to 1090 °C and sintering time is 2.0 to 8.0 hours. The two-stage tempering process is that first tempering is carried out at 890 °C to 920 °C and constant temperature time is 1.5 to 3 hours; and secondary tempering is carried out at 480 °C to 520 °C and constant temperature time is 2 to 6 hours. Since the main phase has a melting point of about 1185 °C and the alloy powder rich in Co generally begins to melt at 600 °C to 750 °C, the NdFeB alloy in a sintering temperature state is composed of a solid main phase, a molten phase rich in Nd, a molten phase rich in B and a molten alloy phase rich in Co, and the molten phases permeate into gaps between solid powder particles of the main phase through methods of liquid-phase flow and molecular thermal movement, so that the alloy phase rich in Co better penetrates to the grain boundary in the main phase.

[0021] The corrosion-resistant sintered NdFeB magnet has the beneficial effects that the Co element in the magnet is more distributed on the grain boundary of the magnet through the innovation of the manufacturing method, the corrosion resistance of the magnet is improved on the basis of ensuring the magnetic property of the magnet, and the sintered NdFeB magnet rich in lanthanum and/or cerium has good corrosion resistance the same as that of an ordinary sintered NdFeB permanent magnet and becomes a rare earth permanent magnet material with practical application value.

Detailed Description of the Invention

[0022] The present invention is further described below with reference to specific embodiments.

Embodiment 1:

[0023]

1, An NdFeB rare earth permanent magnet material rich in lanthanum and/or cerium and with components of $\text{Nd}_{12.3}\text{Ce}_{2.4}\text{Fe}_{\text{remaining}}\text{B}_{6.0}\text{M}_{1.7}$ (at%) is prepared into an NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium by a quick-setting sheet process according to a technical scheme of the present invention;

2, An alloy material rich in Co and with components of $\text{Nd}_{21.72}\text{Pr}_{7.41}\text{Co}_{70.87}$ (at%) is prepared by the quick-setting sheet process;

3, The alloy material rich in Co is added into the NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium at a ratio of 1 wt% for hydrogen breakage, and mixed alloy powder with an average particle diameter of 3.5 μm is obtained by a jet milling process;

4, The mixed alloy powder is pressed and molded to form a square blank of 52 * 52 * 29 (mm) in an orientation magnetic field $\geq 1.5\text{T}$;

5, The molded blank is placed in a high-vacuum sintering furnace for sintering at 1035 °C for 6.0 hours, first tempering at 920 °C for two hours and secondary tempering at 500 °C for 3.5 hours to obtain a corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium.

6, The obtained $\text{Nd}_{12.3}\text{Ce}_{2.4}\text{Fe}_{\text{remaining}}\text{B}_{6.0}\text{M}_{1.7}$ (at%) NdFeB rare earth permanent magnet alloy rich in lanthanum and/or cerium is directly prepared into a sintered NdFeB magnet rich in lanthanum and/or cerium without adding an alloy material rich in Co by using the same manufacturing process.

[0024] The two magnets are machined to obtain $\Phi 10 * 10$ (mm) standard samples, and HAST experiments (131 °C, 96% RH, 2.6bar, 96H) are then conducted to test the corrosion resistance of the materials. The performance of the materials is shown as Table 1.

Table 1 Corrosion resistance test results

Material components (at%, see the components in Embodiment 1)	Mass loss (mg/cm ²)
Sintered NdFeB magnet rich in lanthanum and/or cerium	52.36

(continued)

Material components (at%, see the components in Embodiment 1)	Mass loss (mg/cm ²)
Sintered NdFeB magnet rich in lanthanum and/or cerium with addition of 1 wt% of alloy material rich in Co	0.42

Embodiment 2:

[0025]

1, An NdFeB rare earth permanent magnet material rich in lanthanum and/or cerium and with components of $\text{Pr}_{3.06}\text{Nd}_{8.96}\text{Ce}_{3.31}\text{Fe}_{\text{remaining}}\text{B}_{5.88}\text{M}_{2.25}$ (at%) is prepared into an NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium by a quick-setting sheet process according to the technical scheme of the present invention;

2, An alloy material rich in Co and with components of $\text{Nd}_{23.41}\text{Pr}_{10.97}\text{Co}_{64.24}\text{Zr}_{1.38}$ (at%) is prepared by the quick-setting sheet process;

3, The NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium and the alloy material rich in Co are respectively subjected to hydrogen breaking, in any one period of a jet milling powder preparation process on the NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium, the alloy material rich in Co is added at a ratio of 2wt%, mixed alloy powder having an average particle diameter of 2.8 - 3.0 μm is obtained by powder preparation, and the mixed alloy powder is uniformly mixed by a mixer;

4, The uniformly mixed alloy powder is pressed and molded to form a square blank of 52 * 52 * 29 (mm) in an orientation magnetic field $\geq 1.8\text{T}$;

5, The blank is placed into a high-vacuum sintering furnace for sintering at 1075 °C for 4.0 hours, first tempering at 890 °C for 1.5 hours and secondary tempering at 510 °C for 6.0 hours to obtain a sintered NdFeB magnet rich in lanthanum and/or cerium.

6, The obtained $\text{Pr}_{3.06}\text{Nd}_{8.96}\text{Ce}_{3.31}\text{Fe}_{\text{remaining}}\text{B}_{5.88}\text{M}_{2.25}$ (at%) NdFeB rare earth permanent magnet alloy rich in lanthanum and/or cerium is directly prepared into a sintered NdFeB magnet rich in lanthanum and/or cerium without adding the alloy material rich in Co by using the same manufacturing process.

[0026] The two magnets are machined to prepare $\Phi 10 * 10$ (mm) standard samples, and HAST experiments (131 °C, 96% RH, 2.6bar, 96H) are then performed to test the corrosion resistance of the materials. The performance of the materials is shown as Table 2.

Table 2 Corrosion resistance test results

Material components (at%, see the components in Embodiment 2)	Mass loss (mg/cm ²)
Sintered NdFeB magnet rich in lanthanum and/or cerium	78.25
Sintered NdFeB magnet rich in lanthanum and/or cerium with addition of 2 wt% of alloy material rich in Co	0.88

Embodiment 3:

[0027]

1, An NdFeB rare earth permanent magnet material rich in lanthanum and/or cerium and with components of $\text{Pr}_{2.11}\text{Nd}_{6.18}\text{Ce}_{4.71}\text{Gd}_{0.84}\text{Ho}_{0.6}\text{Fe}_{\text{remaining}}\text{B}_{5.87}\text{M}_{1.08}$ (at%) is prepared into an NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium by a quick-setting sheet process according to the technical scheme of the present invention;

2, An alloy material rich in Co and with components of $\text{Nd}_{36.98}\text{Pr}_{12.62}\text{Co}_{34.47}\text{Cr}_{1.95}\text{Cu}_{3.20}\text{Zn}_{1.55}\text{Al}_{3.76}\text{Nb}_{5.47}$ (at%) is

prepared by the quick-setting sheet process;

3, The NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium and the alloy material rich in Co are respectively subjected to hydrogen breaking, and the NdFeB rare earth permanent magnet alloy is subjected to jet milling powder preparation to obtain permanent magnet alloy powder having an average particle diameter of 3.0 to 3.2 μm ; the alloy material rich in Co is subjected to jet milling powder preparation to obtain alloy powder rich in Co and having an average particle diameter of 4.2 to 4.5 μm , the alloy powder rich in Co is added into the NdFeB rare earth permanent magnet material alloy powder rich in lanthanum and/or cerium at a ratio of 3wt%, and the two types of alloy powder are mixed uniformly by mixing;

4, The uniformly mixed powder is pressed and molded to form a square blank of 52 * 52 * 29 (mm) in an orientation magnetic field $\geq 2.2\text{T}$;

5, The blank is placed into a high-vacuum sintering furnace for sintering at 1060 $^{\circ}\text{C}$ for 8.0 hours, first tempering at 910 $^{\circ}\text{C}$ for 3.0 hours and secondary tempering at 480 $^{\circ}\text{C}$ for 2.0 hours to obtain a sintered NdFeB magnet rich in lanthanum and/or cerium.

6, The obtained $\text{Pr}_{2.11}\text{Nd}_{6.18}\text{Ce}_{4.71}\text{Gd}_{0.84}\text{Ho}_{0.6}\text{Fe}_{\text{remaining}}\text{B}_{5.87}\text{M}_{1.08}$ (at%) NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium is directly prepared into a sintered NdFeB magnet without adding the alloy material rich in Co by using the same manufacturing process.

[0028] The two magnets are machined to prepare $\Phi 10 * 10$ (mm) standard samples, and HAST experiments (131 $^{\circ}\text{C}$, 96% RH, 2.6bar, 96H) are then performed to test the corrosion resistance of the materials. The performance of the materials is shown as Table 3.

Table 3 Corrosion resistance test results

Material components (at%, see the components in Embodiment 3)	Mass loss (mg/cm^2)
Sintered NdFeB magnet rich in lanthanum and/or cerium	88.25
Sintered NdFeB magnet rich in lanthanum and/or cerium with addition of 3 wt% of alloy material rich in Co	0.78

Embodiment 4:

[0029]

1, An NdFeB rare earth permanent magnet material rich in lanthanum and/or cerium and with components of $\text{Nd}_{7.34}\text{Ce}_{5.53}\text{Gd}_{0.41}\text{Fe}_{\text{remaining}}\text{B}_{5.91}\text{M}_{3.32}$ (at%) is prepared into an NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium by a quick-setting sheet process according to the technical scheme of the present invention;

2, An alloy material rich in Co and with components of $\text{Nd}_{77.91}\text{Pr}_{10.71}\text{Co}_{11.38}$ (at%) is prepared by the quick-setting sheet process;

3, The NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium and the alloy material rich in Co are subjected to hydrogen breaking, the NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium is subjected to jet milling powder preparation to obtain NdFeB rare earth permanent magnet material alloy powder rich in lanthanum and/or cerium and having an average particle diameter of 3.4 to 3.6 μm , after powder preparation on the NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium, the alloy material rich in Co is added into a jet mill at a ratio of 4wt% for continuous powder preparation to obtain alloy powder rich in Co having an average particle diameter of 2.5 to 2.7 μm , the alloy powder rich in Co and the NdFeB rare earth permanent magnet material alloy powder are together contained into a barrel, and the two types of alloy powder are mixed uniformly by a three-dimensional mixer;

4, The uniformly mixed powder is pressed and molded to form a square blank of 52 * 52 * 29 (mm) in an orientation magnetic field $\geq 1.5\text{T}$;

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5, The blank is placed into a high-vacuum sintering furnace for sintering at 1060 °C for 3.5 hours, first tempering at 900 °C for 2.0 hours and secondary tempering at 510 °C for 3.5 hours to obtain a sintered NdFeB magnet rich in lanthanum and/or cerium.

6, The obtained $\text{Nd}_{7.34}\text{Ce}_{5.53}\text{Gd}_{0.41}\text{Fe}_{\text{remaining}}\text{B}_{5.91}\text{M}_{3.32}$ (at%) NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium is directly prepared into a sintered NdFeB magnet rich in lanthanum and/or cerium without adding the alloy material rich in Co by using the same manufacturing process.

[0030] The two magnets are machined to prepare $\Phi 10 * 10$ (mm) standard samples, and HAST experiments (131 °C, 96% RH, 2.6bar, 96H) are then performed to test the corrosion resistance of the materials. The performance of the materials is shown as Table 4.

Table 4 Corrosion resistance test results

Material components (at%, see the components in Embodiment 4)	Mass loss (mg/cm ²)
Sintered NdFeB magnet rich in lanthanum and/or cerium	89.31
Sintered NdFeB magnet rich in lanthanum and/or cerium with addition of 4 wt% of alloy material rich in Co	1.01

Embodiment 5:

[0031]

1, An NdFeB rare earth permanent magnet material rich in lanthanum and/or cerium and with components of $\text{Pr}_{2.01}\text{Nd}_{5.88}\text{Ce}_{7.21}\text{Ho}_{0.4}\text{Fe}_{\text{remaining}}\text{B}_{6.21}\text{M}_{0.98}$ (at%) is prepared into an NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium by a quick-setting sheet process according to the technical scheme of the present invention;

2, An alloy material rich in Co and with components of $\text{Nd}_{24.37}\text{Pr}_{8.31}\text{Co}_{60.02}\text{Ga}_{2.54}\text{Nb}_{4.76}$ (at%) is prepared by the quick-setting sheet process;

3, The NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium and the alloy material rich in Co are respectively subjected to hydrogen breaking, and are respectively subjected to jet milling powder preparation to obtain NdFeB rare earth permanent magnet material alloy powder rich in lanthanum and/or cerium and having an average particle diameter of 3.8 to 4.0 μm and alloy powder rich in Co and having an average particle diameter of 2.8 to 3.0 μm , the alloy powder rich in Co is added into the NdFeB rare earth permanent magnet material alloy powder rich in lanthanum and/or cerium at a ratio of 5wt%, and the two types of alloy powder are mixed uniformly by mixing;

4, The mixed powder is pressed and molded to form a square blank of $52 * 52 * 29$ (mm) in an orientation magnetic field $\geq 1.6\text{T}$;

5, The blank is placed into a high-vacuum sintering furnace for sintering at 1090 °C for 2.0 hours, first tempering at 900 °C for 2.5 hours and secondary tempering at 490 °C for 4.0 hours to obtain a sintered NdFeB magnet rich in lanthanum and/or cerium.

6, The obtained $\text{Pr}_{2.01}\text{Nd}_{5.88}\text{Ce}_{7.21}\text{Ho}_{0.4}\text{Fe}_{\text{remaining}}\text{B}_{6.21}\text{M}_{0.98}$ (at%) NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium is directly prepared into a sintered NdFeB magnet rich in lanthanum and/or cerium without adding the alloy material rich in Co by using the same manufacturing process.

[0032] The two magnets are machined to prepare $\Phi 10 * 10$ (mm) standard samples, and HAST experiments (131 °C, 96% RH, 2.6bar, 96H) are then performed to test the corrosion resistance of the materials. The performance of the materials is shown as Table 5.

Table 5 Corrosion resistance test results

Material components (at%, see the components in Embodiment 5)	Mass loss (mg/cm ²)
Sintered NdFeB magnet rich in lanthanum and/or cerium	179.30
Sintered NdFeB magnet rich in lanthanum and/or cerium with addition of 5 wt% of alloy material rich in Co	0.98

Claims

1. A corrosion-resistant sintered neodymium-iron-boron (NdFeB) magnet rich in lanthanum and/or cerium, **characterized by** comprising an NdFeB rare earth permanent magnet material rich in lanthanum and/or cerium and an alloy material rich in Co for improving the corrosion resistance of the material, wherein a component of the NdFeB rare earth permanent magnetic material rich in lanthanum and/or cerium is $\text{Re}_\alpha\text{Fe}_{100-\alpha-\beta-\gamma}\text{B}_\beta\text{M}_\gamma$, wherein Re is a rare earth element, including two or more than two elements selected from La, Ce and Nd, and inevitably containing Nd element; wherein M is an additive element, including one or more than one element selected from Ti, V, Cr, Ni, Zn, Ga, Ge, Al, Zr, Nb, Co, Cu, Ag, Sn, W, Pb, Bi and Pd; wherein Fe is Fe and unavoidable impurities; wherein α , β and γ are the atomic percentage contents of the elements, wherein $12 \leq \alpha \leq 17$, $5.1 \leq \beta \leq 6.8$, and $0.1 \leq \gamma \leq 7.8$; and wherein the alloy material rich in Co includes two or more than two elements selected from Pr, Nd, Gd, Ho, Co, Ti, V, Zn, Ga, Al, Zr, Nb, Cu, Ag, Sn, Pb and Pd, and inevitably contains Co.
2. The corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium according to claim 1, **characterized in that** La and Ce elements in the rare-earth element Re account for 15 wt% to 45 wt% of total use amounts of rare earth in the NdFeB rare earth permanent magnet material rich in lanthanum and/or cerium.
3. The corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium according to claim 1, **characterized in that** the rare earth element Re further comprises one or more than one element selected from Pr, Pm, Sm, Eu, Gd, Ho, Er, Tm, Yb, Lu, Y and Sc.
4. The corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium according to claim 1, **characterized in that** the alloy material rich in Co inevitably does not contain element Fe.
5. A method of manufacturing a corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium, **characterized by** comprising the following specific operation steps:
 - (1) Preparing an NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium according to components of an NdFeB rare earth permanent magnet material rich in lanthanum and/or cerium;
 - (2) Preparing an alloy material rich in Co according to components of the alloy material rich in Co;
 - (3) Breaking the NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium to obtain NdFeB rare earth permanent magnet material alloy powder rich in lanthanum and/or cerium with an average particle size of 2.5 to 4.5 μm ;
 - (4) Adding the alloy material rich in Co obtained in step (2) into the NdFeB rare earth permanent magnet material alloy powder rich in lanthanum and/or cerium according to a certain mass percentage content, wherein the process of pulverizing and mixing the alloy material rich in Co makes the alloy material rich in Co to be uniformly mixed into the NdFeB rare earth permanent magnet material alloy powder rich in lanthanum and/or cerium;
 - (5) Pressing and molding the mixed alloy powder into a blank in an oriented magnetic field $\geq 1.5\text{T}$ under the protection of a nitrogen atmosphere;
 - (6) Placing the molded blank in a high-vacuum sintering furnace for high-temperature sintering, and performing a two-stage tempering process to obtain the corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium.
6. A method of manufacturing a corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium according to claim 5, **characterized in that** a preparation process adopted in step (1) and step (2) is a casting process or a quick-setting sheet process; and in step (3), a breaking method adopted is mechanical breaking or hydrogen breaking plus jet milling.
7. A method of manufacturing a corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium according

to claim 6, **characterized in that** the preparation process adopted in step (1) and step (2) is a quick-setting sheet process.

8. A method of manufacturing a corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium according to claim 7, **characterized in that** a roller speed of a cooling copper roller used in the quick-setting sheet process of step (2) is 5 to 15 times of a roller speed of a cooling copper roller used in the quick-setting sheet process of step (1).

9. A method of manufacturing a corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium according to claim 5, **characterized in that** in step (4), the mass percentage content of the alloy material rich in Co in the 1 NdFeB rare earth permanent magnet material alloy rich in lanthanum and/or cerium is 1% to 5%.

10. A method of manufacturing a corrosion-resistant sintered NdFeB magnet rich in lanthanum and/or cerium according to claim 5, **characterized in that** in step (6), sintering temperature is 1030 °C to 1090 °C, and sintering time is 2.0 to 8.0 hours, and a two-stage tempering process is that first tempering is carried out at 890 °C to 920, and constant temperature time is 1.5 to 3 hours; and secondary tempering is carried out at 480 °C to 520 °C, and constant temperature time is 2 to 6 hours.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2016/101950

A. CLASSIFICATION OF SUBJECT MATTER

H01F 1/057 (2006.01) i; H01F 41/02 (2006.01) i; B22F 3/02 (2006.01) i; B22F 3/10 (2006.01) i
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01F, B22F

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
CNPAT, CNKI, WPI, EPODOC, IEEE: ZHEJIANG DONGYANG, neodymium iron boron, magnet, rare earth, cobalt, lanthanum, cerium, corrosion resistance, main phase, master alloy, auxiliary alloy, grain boundary phase, NdFeB, neodymium, iron, boron, Co, La, Ce, corrosion

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 105427994 A (ZHEJIANG DONGYANG DMEGC RARE EARTH MAGNET CO., LTD.), 23 March 2016 (23.03.2016), claims 1-10	1-10
Y	CN 101958171 A (WUXI TECHNOLOGY DEVELOPMENT CO., LTD. OF NANJING UNIVERSITY OF SCIENCE AND TECHNOLOGY et al.), 26 January 2011 (26.01.2011), description, paragraphs [0018]-[0082], and figure 1	1-10
Y	CN 102280240 A (NANJING UNIVERSITY OF SCIENCE AND TECHNOLOGY et al.), 14 December 2011 (14.12.2011), description, paragraphs [0005]-[0006], and figure 1	1-10
A	CN 103824668 A (ZHEJIANG DONGYANG DMEGC RARE EARTH MAGNET CO., LTD.), 28 May 2014 (28.05.2014), the whole document	1-10
A	CN 102347126 A (SHENYANG GENERAL MAGNETIC CO., LTD.), 08 February 2012 (08.02.2012), the whole document	1-10

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

* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A" document defining the general state of the art which is not considered to be of particular relevance	
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT
 Information on patent family members

International application No.

PCT/CN2016/101950

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN 105427994 A	23 March 2016	None	
CN 101958171 A	26 January 2011	CN 101958171 B	15 February 2012
CN 102280240 A	14 December 2011	CN 102280240 B	25 July 2012
CN 103824668 A	28 May 2014	None	
CN 102347126 A	08 February 2012	CN 102347126 B	23 July 2014
		WO 2012013086 A1	02 February 2012

Form PCT/ISA/210 (patent family annex) (July 2009)