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(54) **HEAVY RARE EARTH-FREE HIGH-PERFORMANCE NEODYMIUM-IRON-BORON PERMANENT MAGNET MATERIAL AND PREPARATION METHOD THEREFOR**

(57) The present application provides a heavy rare earth-free high-performance neodymium iron boron permanent magnet material and a preparation method thereof. The preparation method comprises: providing an anisotropic magnet material which has a chemical formula of $(\text{Nd,Pr})_x\text{Fe}_{(100-x-y-z)}\text{B}_y\text{M}_z$, wherein $28.5\% \leq x \leq 29\%$, $0.86\% \leq y \leq 0.92\%$ and $0 < z \leq 2.5\%$, and M comprises Co, Al, Cu, Zr and other elements; providing an auxiliary phase material which has a chemical formula of $\text{Pr}_a\text{Ni}_{100-b}$, wherein $50\% \leq a \leq 65\%$ and $35\% \leq b \leq 50\%$; and evenly mixing the anisotropic magnet material with the auxiliary phase material to obtain mixed magnetic powders, and then performing orientation profiling, sintering treatment and tempering treatment, so as to obtain the heavy rare earth-free high-performance neodymium iron boron permanent magnet material. The present application can significantly improve the coercivity of the neodymium iron boron permanent magnet material without the use of heavy rare earth while not affecting the mag-

netic property of the neodymium iron boron permanent magnet material, so as to obtain a neodymium iron boron permanent magnet material with excellent magnetic property.

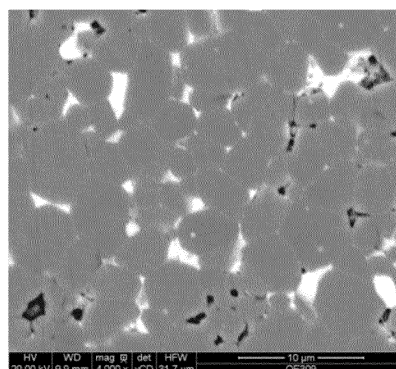


FIG.2

Description**TECHNICAL FIELD**

[0001] The present application relates to a neodymium iron boron permanent magnet material, in particular to a heavy rare earth-free high-performance neodymium iron boron permanent magnet material and a preparation method thereof, belonging to the technical field of rare earth permanent magnet materials.

BACKGROUND

[0002] Sintered neodymium iron boron permanent magnets, referred to as "Magnet King", are permanent magnet materials which have the strongest comprehensive magnetic property in the world nowadays, and have become key basic support materials essential for many modern industry techniques due to their excellent properties and cost performances superior to those of the traditional permanent magnet materials. In recent years, the price of heavy rare earth violently fluctuates, which causes the rare earth permanent magnet industry to worry about heavy rare earth resource supply, so that reduction in the use amount of heavy rare earth and development of heavy rare earth-free high-coercivity magnets become focuses concerned by industrial circles.

[0003] At present, the sintered neodymium iron boron industry generally uses a grain refining technology to achieve research and production of heavy rare earth-free sintered neodymium iron boron magnets. However, as the size of the grains is refined, a series of problems that the magnet is oxidized and processing brittle rupture is formed, etc., are generated during the production. Therefore, large-scale production of heavy rare earth-free sintered neodymium iron boron magnets becomes the most urgent demand and challenge in the neodymium iron boron application market. It is a decisive factor for healthy development of the neodymium iron boron market, and also is a key to the development of the downstream new energy application field.

SUMMARY

[0004] The main objective of the present application is to provide a heavy rare earth-free high-performance neodymium iron boron permanent magnet material and a preparation method thereof in order to overcome the defects in the prior art.

[0005] To achieve the above-mentioned objective, the technical solution adopted in the present application is as follows: An embodiment of the present application provides a preparation method of a heavy rare earth-free high-performance neodymium iron boron permanent magnet material, comprising the following steps:

providing an anisotropic magnet material which has a chemical formula of $(\text{Nd,Pr})_x\text{Fe}_{(100-x-y-z)}\text{B}_y\text{M}_z$, wherein x, y and z each represent the mass percentage of a respective corresponding element, and $28.5\% \leq x \leq 29\%$, $0.86\% \leq y \leq 0.92\%$ and $0 < z \leq 2.5\%$, and M comprises any one or more than two of combinations of Co, Al, Cu and Zr elements;

providing an auxiliary phase material which has a chemical formula of $\text{Pr}_a\text{Ni}_{100-b}$, wherein a and b each represent the mass percentage of a respective corresponding element, and $50\% \leq a \leq 65\%$ and $35\% \leq b \leq 50\%$; and

evenly mixing the anisotropic magnet material with the auxiliary phase material to obtain mixed magnetic powders, and then successively performing orientation profiling, sintering treatment and tempering treatment, so as to obtain the heavy rare earth-free high-performance neodymium iron boron permanent magnet material.

[0006] In some embodiments, the preparation method comprises:

providing a mechanically sprayed material rotary mixing system comprising a spraying system, a feeding system, a stirring system and a rotary mixing mechanism, wherein the stirring system is provided with a dynamic system shaft which is at least used for driving the rotary mixing of the stirring system;

evenly mixing the auxiliary phase material with an organic solvent to obtain an auxiliary organic coating;

putting the anisotropic magnet material into the rotary mixing mechanism in the middle of the stirring system of the mechanically sprayed material rotary mixing system for rotary mixing, and spraying the auxiliary organic coating by using the spraying system so as to mix the anisotropic magnet material with the auxiliary phase material in the stirring system for 1-3 h to obtain the mixed magnetic powders.

[0007] In some embodiments, a method for preparing the auxiliary phase material comprises:

preparing raw materials according to a proportion of each element in the auxiliary phase material;

mixing the prepared raw materials and smelting the mixed material in an inert atmosphere to obtain an auxiliary

phase master alloy;

smashing the auxiliary phase master alloy through hydrogen decrepitation and jet milling or ball milling to prepare the auxiliary phase material.

[0008] In some embodiments, the orientation profiling specifically comprises: performing press molding on the mixed magnetic powders at 2.3 T-2.5 T, and then performing static pressing on the magnetic powders subjected to press molding at 150 MPa-200 MPa to obtain a blank magnet.

[0009] In some embodiments, the sintering treatment specifically comprises: placing the blank magnet subjected to orientation profiling in a vacuum environment and sintering for 2 h-4 h at 1030°C-1060°C to obtain a sintered magnet.

[0010] In some embodiments, the tempering treatment specifically comprises: tempering the sintered magnet obtained by sintering treatment in a vacuum environment or a protective atmosphere, wherein the tempering temperature is 480°C-540°C, and the tempering time is 1 h-3 h.

[0011] An embodiment of the present application further provides the heavy rare earth-free high-performance neodymium iron boron permanent magnet material prepared by using the above-mentioned method.

[0012] Further, the heavy rare earth-free high-performance neodymium iron boron permanent magnet material comprises a main phase structure and a continuous crystal boundary structure distributed around the main phase structure, wherein the crystal boundary structure comprises Pr, Nd, Fe and Ni elements.

[0013] Compared with the prior art, the present application at least has the following beneficial effects:

1) in the preparation method of the heavy rare earth-free high-performance neodymium iron boron permanent magnet material provided by the present application, the coercivity of the neodymium iron boron permanent magnet material can be significantly improved without the use of heavy rare earth while not affecting the magnetic property of the neodymium iron boron permanent magnet material, a neodymium iron boron permanent magnet material with excellent magnetic property can be obtained, the use of heavy rare earth can be avoided, and it is ensured that the coercivity of the neodymium iron boron magnet is obviously improved under the condition of slightly reducing the remanence of the neodymium iron boron magnet, thereby greatly reducing the production cost;

2) in the preparation method of the heavy rare earth-free high-performance neodymium iron boron permanent magnet material provided by the present application, adoption of a formula in which the B content is less than a stoichiometric ratio of neodymium iron boron in combination with introduction of Ni can effectively reduce the ferromagnetic property of a crystal boundary and improve the wettability between the crystal boundary and the main phase, thereby significantly improving the coercivity of the neodymium iron boron permanent magnet material;

3) in the preparation method of the heavy rare earth-free high-performance neodymium iron boron permanent magnet material provided by the present application, the used mechanically sprayed material rotary mixing system can remarkably improve homogeneity of the auxiliary phase mixed with anisotropic magnet powders and improve the magnetic property of the neodymium iron boron permanent magnet material, thereby obtaining a material with excellent magnetic property;

4) the preparation method of the heavy rare earth-free high-performance neodymium iron boron permanent magnet material provided by the present application is simple and feasible, and can be used for industrial production.

BRIEF DESCRIPTION OF THE DRAWINGS

[0014] For more clearly illustrating the embodiments of the present application or technical solution in the prior art, accompanying drawings required to be used in the embodiments or descriptions in the prior art will be simply described below. Obviously, the drawings described below are only some embodiments in the present application, and other drawings can also be made by persons of ordinary skill in the art according to these drawings without creative efforts.

Fig.1 is a scanning electron micrograph of an anisotropic neodymium iron boron permanent magnet material [(Nd-Pr)₂₉Cu_{0.2}Al_{0.1}Zr_{0.2}Co_{0.5}Fe_{bal.}B_{0.9}] without the doping of auxiliary phase powders in comparative example 1;

Fig.2 is a scanning electron micrograph of a neodymium iron boron permanent magnet material obtained in example 1 according to the present application;

Fig.3 is a scanning electron micrograph of a neodymium iron boron permanent magnet material obtained in example 2 according to the present application; and

Fig.4 is a scanning electron micrograph of a neodymium iron boron permanent magnet material obtained in example 3 according to the present application.

DETAILED DESCRIPTION OF THE EMBODIMENTS

[0015] In view of the defects in the prior art, the inventors can put forward the technical solution of the present application

through long-term research and lots of practice, which mainly provides a heavy rare earth-free high-performance neodymium iron boron permanent magnet material and a preparation method thereof. The heavy rare earth-free high-performance neodymium iron boron permanent magnet material has excellent magnetic property and meanwhile is suitable for industrialization. Next, the technical solution, its implementation process and principle will be further explained.

[0016] One aspect of the embodiment of the present application provides a preparation method of a heavy rare earth-free high-performance neodymium iron boron permanent magnet material, comprising the following steps:

providing an anisotropic magnet material which has a chemical formula of $(\text{Nd,Pr})_x\text{Fe}_{(100-x-y-z)}\text{B}_y\text{M}_z$, wherein x, y and z each represent the mass percentage of a respective corresponding element, and $28.5\% \leq x \leq 29\%$, $0.86\% \leq y \leq 0.92\%$ and $0 < z \leq 2.5\%$, the content of B is slightly less than the stoichiometric ratio of neodymium iron boron, and M comprises any one or more than two of combinations of Co, Al, Cu and Zr elements;

providing an auxiliary phase material which has a chemical formula of $\text{Pr}_a\text{Ni}_{100-b}$, wherein a and b each represent the mass percentage of a respective corresponding element, and $50\% \leq a \leq 65\%$ and $35\% \leq b \leq 50\%$; and

evenly mixing the anisotropic magnet material with the auxiliary phase material to obtain mixed magnetic powders, and then successively performing orientation profiling, sintering treatment and tempering treatment, so as to obtain the heavy rare earth-free high-performance neodymium iron boron permanent magnet material.

[0017] In some specific embodiments, the preparation method of the heavy rare earth-free high-performance neodymium iron boron permanent magnet material comprises the following steps:

(1) providing hydrogen decrepitation-jet milling to prepare the anisotropic magnet powders, wherein the chemical formula of the anisotropic magnet powder based on weight percent is $(\text{Nd,Pr})_x\text{Fe}_{(100-x-y-z)}\text{B}_y\text{M}_z$, $28.5\text{wt}\% \leq x \leq 29\text{wt}\%$, $0.86\text{wt}\% \leq y \leq 0.92\text{wt}\%$ and $0 < z \leq 2.5\text{wt}\%$, the content of B is slightly less than the stoichiometric ratio of neodymium iron boron (the magnetic property of the magnet with slightly less B content is superior to that of a normal magnet), and M comprises any one or more than two of combinations of Co, Al, Cu, Zr and the like, but is not limited thereto;

(2) providing auxiliary phase powders, wherein the chemical formula of the auxiliary phase powder based on weight percent is $\text{Pr}_a\text{Ni}_{100-b}$, $50\text{wt}\% \leq a \leq 65\text{wt}\%$ and $35\text{wt}\% \leq b \leq 50\text{wt}\%$;

(3) evenly mixing the anisotropic magnet powders with the auxiliary phase powders through a mechanically sprayed material rotary mixing system to obtain mixed magnetic powders, wherein the mass ratio of the auxiliary phase powders in the mixed magnetic powders is $\geq 0.5 \text{ wt}\%$ and $\leq 6 \text{ wt}\%$; and

(4) successively performing orientation profiling, grade sintering and tempering treatment on the mixed magnetic powders to obtain the heavy rare earth-free high-performance neodymium iron boron permanent magnet material.

[0018] In the preparation method of the heavy rare earth-free high-performance neodymium iron boron permanent magnet material provided by the present application, adoption of a formula in which the B content is less than a stoichiometric ratio of neodymium iron boron in combination with introduction of Ni can effectively reduce the ferromagnetic property of a crystal boundary and improve the wettability between the crystal boundary and the main phase, thereby significantly improving the coercivity of the neodymium iron boron permanent magnet material.

[0019] In some embodiments, in step (1), the hydrogen decrepitation comprises a hydrogen absorption-dehydrogenation process, and during hydrogen decrepitation, the hydrogen absorption temperature is 250°C - 400°C , the hydrogen pressure is 0.1 MPa - 0.35 MPa , preferably 0.2 MPa - 0.3 MPa . To ensure the effect of hydrogen absorption, the hydrogen absorption-dehydrogenation process can be cycled.

[0020] Too high dehydrogenation temperature can lead to change in the phase structure of the crystal boundary, whereas too low dehydrogenation temperature can lead to incomplete dehydrogenation. Therefore, the control of the dehydrogenation temperature can well inhibit the formation of an iron-rich crystal boundary phase. The dehydrogenation temperature can be selected as 350°C - 450°C , and the dehydrogenation time is selected as 5 h - 10 h .

[0021] Through hydrogen absorption-dehydrogenation, the obtained hydrogen decrepitated powder has a hydrogen content of less than 2000 ppm and an average particle size of $80 \mu\text{m}$ - $200 \mu\text{m}$.

[0022] Further, the conditions adopted in jet milling are as follows: the content of oxygen is 200 ppm or less, and the rotation speed of a sorting wheel is 3000 - 5000 r/min .

[0023] In some embodiments, a method for preparing the anisotropic magnet material in step (1) specifically comprises:

preparing raw materials according to a proportion of each element in the anisotropic magnet material;

mixing the prepared raw materials and smelting the mixed material in an inert atmosphere to obtain a master alloy; rapidly hardening the master alloy to form an alloy slice; and

smashing the alloy slice through hydrogen decrepitation and jet milling to prepare the anisotropic magnet powders, wherein the chemical formula of the anisotropic magnet powder is $(\text{Nd,Pr})_x\text{Fe}_{(100-x-y-z)}\text{B}_y\text{M}_z$, $28.5\text{wt}\% \leq x \leq 29\text{wt}\%$,

0.86wt% $\leq$ y $\leq$ 0.92wt% and O<z<2.5wt%, the content of B is slightly less than the stoichiometric ratio of neodymium iron boron, and M comprises at least one of Co, Al, Cu and Zr.

[0024] Further, the anisotropic magnet material has a particle size of 1.5 μ m-3.5 μ m.

[0025] In some embodiments, a method for preparing the auxiliary phase material in step (2) specifically comprises:

preparing raw materials according to a proportion of each element in the auxiliary phase material;
mixing the prepared raw materials and smelting the mixed material in an inert atmosphere to obtain an auxiliary phase master alloy; and
smashing the auxiliary phase master alloy through hydrogen decrepitation and jet milling or a ball milling process to prepare the auxiliary phase material.

[0026] Further, the auxiliary phase material has a particle size of 0.1 μ m-3 μ m.

[0027] Further, the hydrogen decrepitation comprises a hydrogen absorption-dehydrogenation process, and during hydrogen decrepitation, the hydrogen absorption temperature is 250°C-400°C, the hydrogen pressure is 0.1 MPa-0.35 MPa, preferably 0.2 MPa-0.3 MPa. To ensure the effect of hydrogen absorption, the hydrogen absorption-dehydrogenation process can be cycled.

[0028] Too high dehydrogenation temperature can lead to change in the phase structure of the crystal boundary, whereas too low dehydrogenation temperature can lead to incomplete dehydrogenation. Therefore, the control of the dehydrogenation temperature can well inhibit the formation of an iron-rich crystal boundary phase. The dehydrogenation temperature can be selected as 350°C-450°C, and the dehydrogenation time is selected as 5 h-10 h.

[0029] Through hydrogen absorption-dehydrogenation, the obtained hydrogen decrepitated powder has a hydrogen content of less than 2000 ppm and an average particle size of 80 μ m-200 μ m.

[0030] Further, the conditions adopted in jet milling are as follows: the content of oxygen is 100 ppm or less, and the rotation speed of a sorting wheel is 3000-5000 r/min.

[0031] Further, the conditions adopted in ball milling are as follows: the rotation speed of ball milling is 50-200 Hz under the protection of alcohols.

[0032] In some embodiments, step (3) specifically comprises:

providing a mechanically sprayed material rotary mixing system comprising a spraying system, a feeding system, a stirring system and a rotary mixing mechanism, wherein the stirring system is provided with a dynamic system shaft which is at least used for driving the rotary mixing of the stirring system;
evenly mixing the auxiliary phase material with an organic solvent to obtain an auxiliary organic coating; and
putting the anisotropic magnet material into the rotary mixing mechanism in the middle of the stirring system of the mechanically sprayed material rotary mixing system for rotary mixing, and spraying the auxiliary organic coating by using the spraying system so as to mix the anisotropic magnet material with the auxiliary phase material in the stirring system for 1-3 h to obtain the mixed magnetic powders.

[0033] In the preparation method of the heavy rare earth-free high-performance neodymium iron boron permanent magnet material provided by the present application, the used mechanically sprayed material rotary mixing system can remarkably improve the homogeneity of the auxiliary phase mixed with the anisotropic magnet powders and improve the magnetic property of the neodymium iron boron permanent magnet material, thereby obtaining a material with excellent magnetic property.

[0034] Further, the mass ratio of the auxiliary phase material to the organic solvent is 1:4-1:10.

[0035] Further, the organic solvent comprises an alcohol solvent (such as ethanol and ethylene glycol) and an alkane solvent (such as tetrachloromethane and n-hexane), but is not limited thereto.

[0036] Further, the mass ratio of the anisotropic magnet material to the auxiliary phase material is 99.5:0.5-94:6.

[0037] Further, the content of the auxiliary phase material in the mixed magnetic powders is 0.5 wt%-6 wt%.

[0038] In some more preferred embodiments, the step (3) specifically comprises:

providing a mechanically sprayed material rotary mixing system comprising a spraying system, wherein the spraying system is provided with a feeding system, the lower part of the spraying system is equipped with a stirring system, a rotary mixing mechanism is mounted in the middle of the stirring system, the stirring system is provided with a dynamic system shaft, and the stirring system is driven by the dynamic system shaft to perform rotary mixing so as to achieve the spraying and mixing process;
mixing the auxiliary phase powders with the organic solvent in a weight ratio of 1:4-1:10 to obtain an auxiliary phase organic coating, wherein the organic solvent is an alcohol solvent, an alkane solvent, or the like; and
putting the anisotropic magnet powders into the stirring system of the mechanically sprayed material rotary mixing

system for rotary mixing, and spraying the auxiliary organic coating, wherein the anisotropic magnet powders are mixed with the auxiliary phase powders for 1-3 h in a mass ratio of 99.5:0.5-94:6.

[0039] In some embodiments, the orientation profiling in step (4) specifically comprises: performing press molding on the mixed magnetic powders at 2.3 T-2.5 T, and then performing static pressing on the magnetic powders subjected to press molding at 150 MPa-200 MPa to obtain a blank magnet.

[0040] In some embodiments, the sintering treatment in step (4) specifically comprises: after the mixed magnetic powders are subjected to orientation profiling, placing the blank magnet obtained by orientation profiling into a vacuum environment and performing grade sintering at a low temperature (a degassing for sintering thermal treatment: for example, performing heat preservation for 2 h at 320°C, and performing heat preservation for 2 h at 550°C), removing volatile substances, and sintering for 2 h -4 h at 1030°C-1060°C to obtain a sintered magnet.

[0041] Further, during the sintering, the vacuum degree of the furnace body is 3×10^{-3} Pa or less to avoid the oxidization phenomenon of the neodymium iron boron permanent magnet material.

[0042] In some embodiments, the tempering treatment in step (4) specifically comprises: tempering the sintered magnet obtained by sintering treatment in a vacuum environment or a protective atmosphere, wherein the temperature of tempering treatment is 480°C-540°C and the time of tempering treatment is 1 h-3 h.

[0043] Another aspect of the embodiment of the present application also provides the heavy rare earth-free high-performance neodymium iron boron permanent magnet material prepared by using the above-mentioned method.

[0044] Further, the heavy rare earth-free high-performance neodymium iron boron permanent magnet material comprises a main phase structure and a continuous crystal boundary structure distributed around the main phase structure, and improves the wettability between the crystal boundary and the crystalline grains of the main phase. The crystal boundary structure comprises an antiferromagnetic structure formed of Pr, Nd, Fe and Ni, which can effectively reduce the ferromagnetism of the entire crystal boundary.

[0045] In conclusion, the preparation method adopted by the present application can not only obtain the high-performance neodymium iron boron permanent magnet material but also avoid the use of heavy rare earth, so that the coercivity of the neodymium iron boron permanent magnet material is significantly improved under the condition of ensuring the slightly reduced remanence of the neodymium iron boron magnet, thereby greatly reducing the production cost. Furthermore, the preparation method of the high-performance neodymium iron boron permanent magnet material provided by the present application is simple and feasible, and can be used for industrial production.

[0046] To make the objectives, technical solution and advantages of the present application more clear, the technical solutions in embodiments of the present application will be described in detail in combination with drawings in embodiments of the present application. Obviously, the described embodiments are only some embodiments of the present application but not all the embodiments. Based on the embodiments of the present application, all of the other embodiments obtained by persons of ordinary skill in the art without creative efforts should be included within the protective scope of the present application.

Example 1

[0047] In this example, the chemical formula of the anisotropic magnetic powder is $(\text{Nd-Pr})_{29}\text{Cu}_{0.2}\text{Al}_{0.4}\text{Zr}_{0.15}\text{Co}_1\text{Fe}_{\text{bal.}}\text{B}_{0.89}$, the chemical formula of the auxiliary phase powder is $\text{Pr}_{62.5}\text{Ni}_{37.5}$, and the doping amount of the auxiliary phase powder is 1% of the amount of the mixed magnetic powder.

1) The raw materials with a purity of greater than 99% were proportioned according to the nominal composition mass percentage of $(\text{NdPr})_{29}\text{Cu}_{0.2}\text{Al}_{0.4}\text{Zr}_{0.15}\text{Co}_1\text{Fe}_{\text{bal.}}\text{B}_{0.89}$, alloy slices with a thickness of about 0.4 mm were prepared by rapid hardening, and the anisotropic magnetic powders with an average particle size of 2.2 μm were prepared by performing hydrogen decrepitation and jet milling on the alloy slices. The scanning electron micrograph of the anisotropic magnetic powder is shown in Fig.1.

2) The auxiliary phase alloy was proportioned according to the mass percentage of the nominal composition $\text{Pr}_{62.5}\text{Ni}_{37.5}$, and powders with an average particle size of 1.5 μm were prepared by smelting, hydrogen decrepitation and jet milling.

3) The auxiliary phase powders $\text{Pr}_{62.5}\text{Ni}_{37.5}$ and the anisotropic magnetic powders were proportioned in a ratio of 1:99 and then mixed for 3 h in a mechanically sprayed material rotary mixing system. The evenly mixed powders were subjected to press molding in an orientation field at 2 T and then underwent isostatic cool pressing in hydraulic oil at 200 MPa to obtain a blank magnet.

4) The blank magnet was subjected to grade sintering for 2 h in a vacuum sintering furnace and cooled to room temperature by gas quenching in combination with air cooling. Subsequently, the above cooled blank magnet was tempered for 2 h at 500°C, then cooled to room temperature through gas quenching in combination with air cooling and then discharged, so as to obtain a heavy rare earth-free high-performance neodymium iron boron permanent

magnet material.

[0048] The prepared neodymium iron boron permanent magnet material was tested. Relative to a permanent magnet material without the doping of the auxiliary phase magnet powders, the obtained neodymium iron boron permanent magnet material has the coercivity H_{cj} which is increased by 2.54 kOe and the remanence B_r which is reduced by 0.18 kGs. The scanning electron micrograph of the obtained neodymium iron boron permanent magnet material is shown in Fig.2.

Comparative example 1

[0049] This comparative example is different from example 1 that the auxiliary phase powders are not doped.

Example 2

[0050] This preparation method is basically the same as that in example 1, and the difference is that the doping amount of the auxiliary phase powders is 2% of the amount of the mixed magnetic powders, and the remained process conditions are seen in Table 1.

[0051] The prepared neodymium iron boron permanent magnet material was tested. Relative to a permanent magnet material without doping of the auxiliary phase magnet powders, the obtained neodymium iron boron permanent magnet material has the coercivity H_{cj} which is increased by 3.70 kOe and the remanence B_r which is reduced by 0.27 kGs. The scanning electron micrograph of the obtained neodymium iron boron permanent magnet material is shown in Fig.3.

Example 3

[0052] This preparation method is basically the same as that in example 1, and the difference is that the doping amount of the auxiliary phase powders is 4% of the amount of the mixed magnetic powders, and the remained process conditions are seen in Table 1.

[0053] The prepared neodymium iron boron permanent magnet material was tested. Relative to a permanent magnet material without doping of the auxiliary phase magnet powders, the obtained neodymium iron boron permanent magnet material has the coercivity H_{cj} which is increased by 4.89 kOe and the remanence B_r which is reduced by 0.6 kGs. The scanning electron micrograph of the obtained neodymium iron boron permanent magnet material is shown in Fig.4.

Examples 4-6

[0054] The preparation steps of anisotropic magnet powders and auxiliary phase powders in these examples are basically consistent to those in example 1, and the difference is that reaction conditions, such as the addition proportions of the used auxiliary phase powders, the average particle size of the anisotropic magnet powders, the average particle size of the auxiliary phase powders, the temperature and time of the mechanically sprayed material rotary mixing and sintering, and the temperature and time of tempering treatment, are specifically seen in Table 1 below, and the obtained products and their properties are seen in Table 2 below.

Table 1 Reaction conditions in examples 1-6

Examples		1	2	3	4	5	6
Process parameters							
Addition proportion of auxiliary phase powders	%	1	2	4	0.5	5	6
Anisotropic magnetic powders	Average particle size (μm)	2.2	2.5	2.8	2.5	3	2
Auxiliary phase powders	Average particle size (μm)	1.5	1.8	2	2	3	0.1
Steps 1) and 2) hydrogen decrepitation	Hydrogen absorption temperature (°C)	250	280	300	320	350	400
	Hydrogen pressure (MPa)	0.1	0.2	0.15	0.18	0.3	0.35
	Dehydrogenation temperature (°C)	350	360	400	380	450	420

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	Dehydrogenation time (h)	10	9	6	8	5	6
Step 1) jet milling	Oxygen content	200	150	100	120	80	180
	Rotation speed of sorting wheel	4500	4000	3800	4000	3000	5000
Step 2) jet milling	Oxygen content	100	50	100	60	80	70
	Rotation speed of sorting wheel	4000	3800	3500	3500	3000	5000
Mechanically sprayed material rotary mixing	Stirring and mixing time (h)	3	3	3	2	3	1
Sintering and tempering treatments	Sintering temperature (°C)	1040	1045	1048	1030	1055	1060
	Sintering time (h)	2	2	2	4	3	3
	Tempering temperature (°C)	500	480	500	530	540	520
	Tempering time (h)	2	3	2	1	2	2

Table 1 Magnetic properties of neodymium iron boron magnets prepared in examples 1-6 and comparative example 1

Types of magnets	Br (kGs)	Hcj (kOe)	(BH) _m (MGOe)
Comparative example 1	13.93	15.08	47.11
Example 1	13.75	17.62	45.38
Example 2	13.66	18.78	44.90
Example 3	13.33	19.97	42.61
Example 4	13.85	16.5	46.35
Example 5	13.01	20.84	41.02

(continued)

Types of magnets	Br (kGs)	H _{cj} (kOe)	(BH) _m (MGOe)
Example 6	12.75	22.03	38.98

[0055] It can be seen from Table 2 that the coercivity of the iron boron permanent magnet material obtained in comparative example 1 is obviously inferior to that in examples 1-6.

Example 7

[0056] This preparation method is basically the same as that in example 1, and the difference is that in this example, the chemical formula of the anisotropic magnetic powder is $(\text{NdPr})_{28.5}\text{Cu}_{0.6}\text{Al}_{0.4}\text{Zr}_{0.5}\text{Co}_1\text{Fe}_{\text{bal.}}\text{B}_{0.89}$, and the chemical formula of the auxiliary phase powder is PresNiss.

Example 8

[0057] This preparation method is basically the same as that in example 1, and the difference is that in this example, the chemical formula of the anisotropic magnetic powder is $(\text{NdPr})_{28.8}\text{Cu}_{0.3}\text{Al}_{0.5}\text{Zr}_{0.15}\text{Co}_1\text{Fe}_{\text{bal.}}\text{B}_{0.90}$, and the chemical formula of the auxiliary phase powder is $\text{Pr}_{50}\text{Ni}_{50}$.

[0058] By test, the magnetic properties of the neodymium iron boron permanent magnet materials obtained in examples 7-8 are basically consistent to those in example 1, and the coercivities of the neodymium iron boron permanent magnet material obtained in examples 7-8 are both higher than that in comparative example 1.

[0059] To sum up, by virtue of the above technical solution of the present application, the present application can not only obtain the high-performance neodymium iron boron permanent magnet material but also avoid the use of the heavy rare earth, and can ensure that the coercivity of the neodymium iron boron magnet is significantly improved under the condition of ensuring the slightly reduced remanence of the neodymium iron boron magnet, thereby greatly reducing the production cost.

[0060] Various aspects, embodiments, features and examples of the present application should be deemed as being illustrative in all the aspects and are not intended to limit the present application, and the scope of the present application is only defined by claims. Without departing from the spirit and scope of the claimed present application, those skilled in the art will understand other embodiments, amendments and uses.

[0061] Use of the title and chapters in the present application is not meant to limit the present application; each chapter can be applied to any aspects, embodiments or features of the present application.

[0062] Throughout the present application, the composition can be described as having, comprising or including specific components or the process is described as having, comprising or including specific process steps, it is expected that the composition taught by the present application especially consists or consists of the described components, and the process taught by the present application especially consists or consists of the described process steps.

[0063] It should be understood that the order of each step or the order of implementing specific action is not extremely important, as long as operation is conducted according to the teaching of the present application. In addition, two or more than two steps or actions can be simultaneously conducted.

[0064] Moreover, the inventors of this case perform corresponding tests by replacing corresponding process conditions in examples 1-3 with other process conditions listed above, the contents required to be verified are close to those of products in examples 1-3. Therefore, the verified content of each embodiment is not illustrated one by one herein, and the advantages of the present application are stated by only taking examples 1-3 as representatives.

[0065] Although the present application has been described by reference to illustrative embodiments, those skilled in the art will understand that various other variations, omitting and/or addition can be made without departing from the spirit and scope of the present application and elements in embodiments can be replaced with substantive equivalents. In addition, many amendments can be made without departing from the scope of the present application to make specific situations or materials adapt to the teaching of the present application. Therefore, it is herein intended to render the present application to include all the embodiments belonging to the scope of the appended claims rather than to limit the present application to specific embodiments disclosed for implementing the present application.

Claims

1. A preparation method of a heavy rare earth-free high-performance neodymium iron boron permanent magnet material, comprising the following steps:

providing an anisotropic magnet material which has a chemical formula of $(\text{Nd,Pr})_x\text{Fe}_{(100-x-y-z)}\text{B}_y\text{M}_z$, wherein x, y and z each represent the mass percentage of a respective corresponding element, and $28.5\% \leq x \leq 29\%$, $0.86\% \leq y \leq 0.92\%$ and $0 < z \leq 2.5\%$, and M comprises any one or more than two of combinations of Co, Al, Cu and Zr elements;

providing an auxiliary phase material which has a chemical formula of $\text{Pr}_a\text{Ni}_{100-b}$, wherein a and b each represent the mass percentage of a respective corresponding element, and $50\% \leq a \leq 65\%$ and $35\% \leq b \leq 50\%$; and evenly mixing the anisotropic magnet material with the auxiliary phase material to obtain mixed magnetic powders, and then successively performing orientation profiling, sintering treatment and tempering treatment, so as to obtain the heavy rare earth-free high-performance neodymium iron boron permanent magnet material.

2. The preparation method according to claim 1, wherein a method for preparing the anisotropic magnet material comprises:

preparing raw materials according to a proportion of each element in the anisotropic magnet material; mixing the prepared raw materials and smelting the mixed material in an inert atmosphere to obtain a master alloy; rapidly hardening the master alloy to form an alloy slice; and smashing the alloy slice through hydrogen decrepitation and jet milling to prepare the anisotropic magnet material.

3. The preparation method according to claim 1 or 2, wherein the anisotropic magnet material has a particle size of $1.5\ \mu\text{m}$ - $3.5\ \mu\text{m}$; and/or, the hydrogen decrepitation comprises a hydrogen absorption-dehydrogenation process, and the hydrogen absorption temperature is 250°C - 400°C , the hydrogen pressure is $0.1\ \text{MPa}$ - $0.35\ \text{MPa}$, preferably $0.2\ \text{MPa}$ - $0.3\ \text{MPa}$, the dehydrogenation temperature is 350°C - 450°C , and the dehydrogenation time is 5-10 h; preferably, the hydrogen decrepitated powder obtained by the hydrogen decrepitation has a hydrogen content of less than 2000 ppm and an average particle size of $80\ \mu\text{m}$ - $200\ \mu\text{m}$; and/or, the conditions adopted in jet milling are as follows: the content of oxygen is 200 ppm or less, and the rotation speed of a sorting wheel is 3000-5000 r/min.

4. The preparation method according to claim 1, wherein a method for preparing the auxiliary phase material comprises:

preparing raw materials according to a proportion of each element in the auxiliary phase material; mixing the prepared raw materials and smelting the mixed material in an inert atmosphere to obtain an auxiliary phase master alloy; and smashing the auxiliary phase master alloy through hydrogen decrepitation and jet milling or ball milling to prepare the auxiliary phase material.

5. The preparation method according to claim 4, wherein the auxiliary phase material has a particle size of $0.1\ \mu\text{m}$ - $3\ \mu\text{m}$; and/or the hydrogen decrepitation comprises a hydrogen absorption-dehydrogenation process, and the hydrogen absorption temperature is 250°C - 400°C , the hydrogen pressure is $0.1\ \text{MPa}$ - $0.35\ \text{MPa}$, preferably $0.2\ \text{MPa}$ - $0.3\ \text{MPa}$, the dehydrogenation temperature is 350°C - 450°C , and the dehydrogenation time is 5-10 h; preferably, the hydrogen decrepitated powder obtained by the hydrogen decrepitation has a hydrogen content of less than 2000 ppm and an average particle size of $80\ \mu\text{m}$ - $200\ \mu\text{m}$; and/or, the conditions adopted in jet milling are as follows: the content of oxygen is 100 ppm or less, and the rotation speed of a sorting wheel is 3000-5000 r/min; and the conditions adopted in the ball milling are as follows: the rotation speed of ball milling is 50-200 Hz under the protection of alcohols.

6. The preparation method according to claim 1, comprising:

providing a mechanically sprayed material rotary mixing system comprising a spraying system, a feeding system, a stirring system and a rotary mixing mechanism, wherein the stirring system is provided with a dynamic system shaft which is at least used for driving the rotary mixing of the stirring system;

evenly mixing the auxiliary phase material with an organic solvent to obtain an auxiliary organic coating; and putting the anisotropic magnet material into the rotary mixing mechanism in the middle of the stirring system of the mechanically sprayed material rotary mixing system for rotary mixing, and spraying the auxiliary organic coating by using the spraying system so as to mix the anisotropic magnet material with the auxiliary phase material in the stirring system for 1-3 h to obtain the mixed magnetic powders.

7. The preparation method according to claim 6, wherein a mass ratio of the auxiliary phase material to the organic solvent is 1:4-1:10; and/or the organic solvent comprises an alcohol solvent and/or an alkane solvent; preferably, the alcohol solvent comprises ethanol and/or ethylene glycol; preferably, the alkane solvent comprises tetrachlo-

romethane and/or n-hexane; and/or a mass ratio of the anisotropic magnet material to the auxiliary phase material is 99.5:0.5-94:6; and/or the content of the auxiliary phase material in the mixed magnetic powder is 0.5 wt%-6 wt%.

- 5 **8.** The preparation method according to claim 1, wherein the orientation profiling specifically comprises: performing press molding on the mixed magnetic powders at 2.3 T-2.5 T, and then performing static pressing on the magnetic powders subjected to press molding at 150 MPa-200 MPa to obtain a blank magnet;

and/or, the sintering treatment specifically comprises: placing the blank magnet subjected to orientation profiling in a vacuum environment and sintering for 2 h-4 h at 1030°C-1060°C to obtain a sintered magnet; preferably, 10 the vacuum degree of the vacuum environment is 3×10^{-3} Pa or less;

and/or, the tempering treatment specifically comprises: tempering the sintered magnet obtained by sintering treatment in a vacuum environment or a protective atmosphere, wherein the tempering environment is 480°C-540°C, and the tempering time is 1 h-3 h.

- 15 **9.** A heavy rare earth-free high-performance neodymium iron boron permanent magnet material prepared by using the method according to any one of claims 1-8.

- 20 **10.** The heavy rare earth-free high-performance neodymium iron boron permanent magnet material according to claim 9, the heavy rare earth-free high-performance neodymium iron boron permanent magnet material comprising a main phase structure and a continuous crystal boundary structure distributed around the main phase structure, wherein the crystal boundary structure comprises Pr, Nd, Fe and Ni elements.

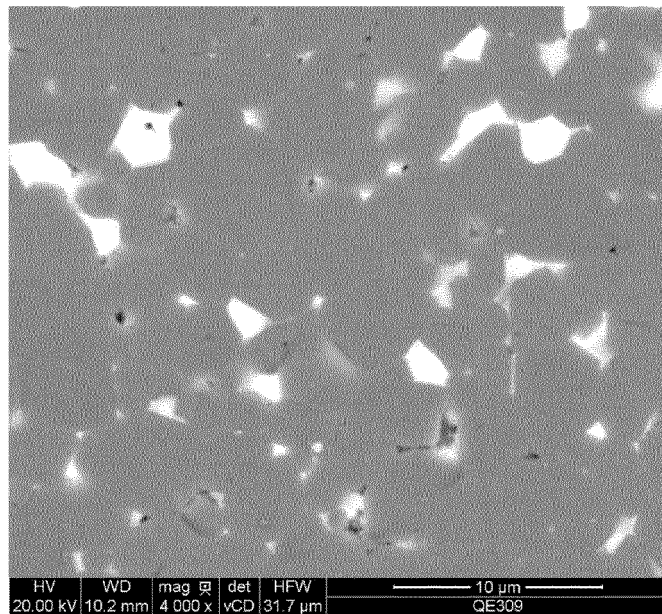


FIG.1

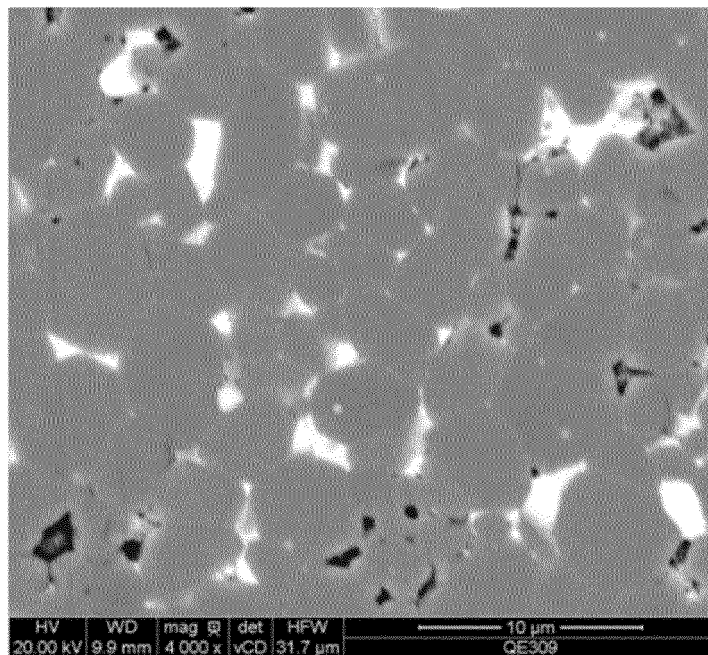


FIG.2

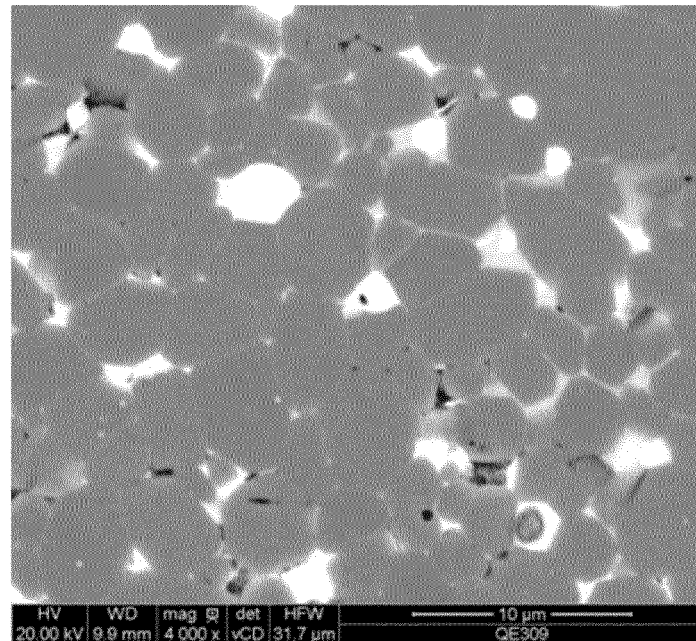


FIG.3

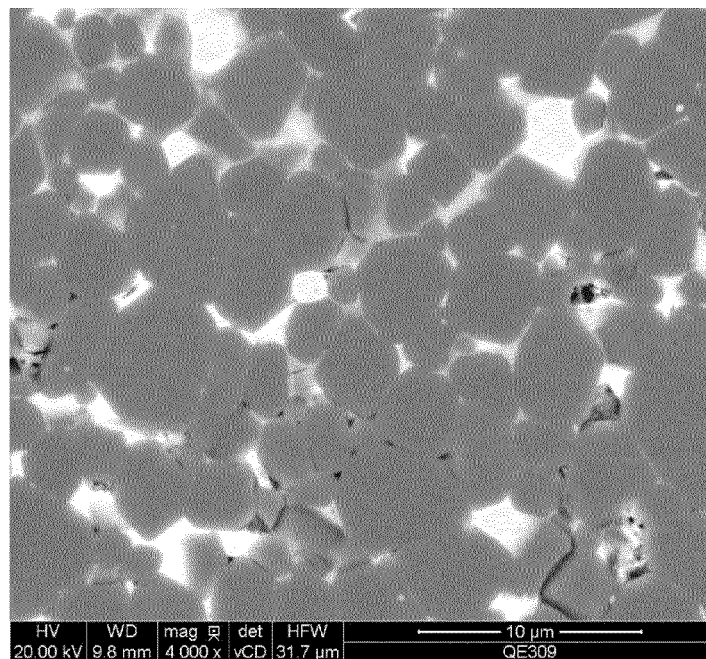


FIG.4

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2020/097637

5	A. CLASSIFICATION OF SUBJECT MATTER		
	H01F 1/057(2006.01)i; H01F 41/02(2006.01)i		
	According to International Patent Classification (IPC) or to both national classification and IPC		
	B. FIELDS SEARCHED		
10	Minimum documentation searched (classification system followed by classification symbols)		
	H01F		
	Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
15	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
	CNKI, CNABS, DWPI, SIPOABS: 永磁, 磁体, 钕铁硼, 各向异性, 辅相材料, 磁粉, 百分比, 压型, 烧结, 回火, 镍, 钴, 铜, 锆, 钽, 钼, permanent, magnet, neodymium, iron, boron, anisotropic, auxiliary, material, magnetic powder, percentage, pressed, sintered, heat-treated, Nd, Pr, B, Co, Al, Cu, Zr, Ni		
	C. DOCUMENTS CONSIDERED TO BE RELEVANT		
20	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	A	CN 109545491 A (NINGBO INSTITUTE OF MATERIALS TECHNOLOGY AND ENGINEERING, CHINESE ACADEMY OF SCIENCES) 29 March 2019 (2019-03-29) entire document	1-10
25	A	CN 101740190 A (MIANYANG WESTMAG MAGNETISM & ELECTRICITY CO., LTD.) 16 June 2010 (2010-06-16) entire document	1-10
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30	A	CN 103632834 A (JIANGSU UNIVERSITY) 12 March 2014 (2014-03-12) entire document	1-10
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35	A	EP 0395625 A2 (BOEHLER GMBH et al.) 31 October 1990 (1990-10-31) entire document	1-10
	☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
40	* Special categories of cited documents: "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 "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) "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 "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 "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 "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 "&" document member of the same patent family		
45			
	Date of the actual completion of the international search		Date of mailing of the international search report
	15 March 2021		24 March 2021
50	Name and mailing address of the ISA/CN		Authorized officer
	China National Intellectual Property Administration (ISA/CN) No. 6, Xitucheng Road, Jimenqiao, Haidian District, Beijing 100088 China		
55	Facsimile No. (86-10)62019451		Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Information on patent family members

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