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(54) **SURFACE TREATMENT METHOD FOR RARE EARTH MAGNETIC POWDER, AND INJECTION MOLDED RARE EARTH MAGNETIC MATERIAL AND PREPARATION METHOD THEREFOR**

(57) Provided are a surface treatment method of rare earth magnetic powder, an injection molding rare earth magnetic material and a preparation method thereof. The above surface treatment method includes: step S1, adding rare earth magnetic powder to weak acid solution, as to weakly acidify the surface of the rare earth magnetic powder, to form weakly acidified magnetic powder, herein a weak acid in the weak acid solution is an inorganic weak acid with an acidity coefficient pKa value greater than 4.5 and/or an organic weak acid with an acidity coefficient greater than 1.0; step S2, phosphating the weak-

ly acidified magnetic powder with phosphating solution, to form phosphating magnetic powder; and step S3, mixing the phosphating magnetic powder with a coupling agent, as to coupling-treat the phosphating magnetic powder, and then drying, to obtain the rare earth magnetic powder after surface treatment. The present disclosure solves a problem in an existing technology that that the rare earth magnetic powder has weak oxidation resistance, so that the rare earth magnetic material after injection molding is poor in magnetic performance.

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Description**Technical Field**

[0001] The present disclosure relates to the field of rare earth permanent magnets, in particular to a surface treatment method of rare earth magnetic powder, an injection molding rare earth magnetic material and a preparation method thereof.

Background

[0002] An injection molding magnet is made by melting, blending, extruding and granulating organic polymer resin and magnetic powder. Commonly used polymer resins include polyamide PA6, PA66, PA12, PA11, and PA612 series and polyphenylene sulfide (PPS) with the better temperature resistance, polyether ether ketone (PEEK) and the like; the magnetic powder include a lower-performance ferrite (FeO) and higher-performance rare earths magnetic powder: neodymium iron boron (Nd-Fe-B), samarium iron nitrogen (Sm-Fe-N), samarium cobalt (Sm-Co) and the like. As the market is continuously evolved, the requirements for performance and product miniaturization are higher and higher, and the demands for the injection molding rare earth magnetic material are greater and greater. However, the rare earth magnetic powder is different from ferrite powder, and the rare earth magnetic powder itself belongs to alloy powder. In a granulation process, due to the higher temperature required, the magnetic powder is extremely easy to be oxidized, so that the performance thereof is significantly reduced, especially the rare earth powder with the finer powder particle size, such as anisotropic SmFeN powder. In a powder-making process, in order to improve the magnetic performance of the anisotropic SmFeN powder, manufacturers often use a method for adjusting the powder particle size, so that a large amount of ultra-fine powder is generated, the particle size of this ultra-fine powder often only reaches 1-2 μm , and this powder is extremely easy to be oxidized, at the same time, a spontaneous combustion situation may even occur while it is exposed in the high temperature air.

[0003] Therefore, in order to prepare a high-performance injection molding rare earth magnetic raw material, it is usually necessary to firstly perform the surface treatment on the rare earth magnetic powder to provide a protective layer on the surface of the magnetic powder, so that the oxidation of the magnetic powder may be reduced in a treatment process, and the magnetic performance thereof is protected. At present, many companies use a mode of coupling-treatment to treat the surface of magnetic powder, and the coupling-treatment mode may improve the bondability with binders PA and PPS. After the binder is dissolved in a double-screw extruder, it wraps the magnetic powder, the magnetic powder inside the binder may be protected from being oxidized, but before the binder completely wraps the magnetic powder, the magnetic powder may still be oxidized to a large extent. A patent CN201510454107.8 also mentions a method of treating rare earth SmFeN magnetic powder by immersing the magnetic powder in coupling agent and phosphoric acid composite solution. Through phosphoric acid solution, a certain phosphating film may be formed on the surface of the powder, thereby the high temperature resistance of the magnetic powder is improved, and the magnetic powder is protected from being oxidized during a granulation process. A phosphoric acid forms a phosphate crystal nucleus on an active site of the surface of the magnetic powder, and then the crystal nucleus continues to grow, to form the stable phosphating film. The quality and integrity of the phosphating film are greatly related to the number of the active points on the surface of the magnetic powder. If it is simply immersed in the phosphoric acid solution, the active site on the surface of the magnetic powder is very weak, and it is difficult to form the stable and high-quality phosphating film, so that in the subsequent high-temperature granulation process, the rare earth magnetic powder after the treatment still has a risk of being oxidized to a large extent.

[0004] Based on the above reasons, it is necessary to provide a new surface treatment method of rare earth magnetic powder, so that it has the better oxidation resistance, and the magnetic performance of the rare earth magnetic material after the injection molding thereof is improved.

Summary

[0005] A main purpose of the present disclosure is to provide a surface treatment method of rare earth magnetic powder, an injection molding rare earth magnetic material and a preparation method thereof, as to solve a problem in an existing technology that the rare earth magnetic powder has weak oxidation resistance, so that the rare earth magnetic material after injection molding is poor in magnetic performance.

[0006] In order to achieve the above purpose, according to one aspect of the present disclosure, a surface treatment method of rare earth magnetic powder is provided, and it includes the following steps: step S1, adding rare earth magnetic powder to weak acid solution, as to weakly acidify the surface of the rare earth magnetic powder, to form weakly acidified magnetic powder, herein a weak acid in the weak acid solution is an inorganic weak acid with an acidity coefficient pK_a value greater than 4.5 and/or an organic weak acid with an acidity coefficient greater than 1.0; step S2, phosphating the

weakly acidified magnetic powder with phosphating solution, to form phosphating magnetic powder; and step S3, mixing the phosphating magnetic powder with a coupling agent, as to coupling-treat the phosphating magnetic powder, and then drying, to obtain a surface treated rare earth magnetic powder.

[0007] Further, the weak acid is one or more of an oxalic acid, an acetic acid and a carbonic acid; preferably, a pH value of the weak acid solution is 5-7; preferably, ethanol is used to adjust the pH value of the weak acid solution; and preferably, a volume ratio of the weak acid solution to the rare earth magnetic powder is 1.5-3:1.

[0008] Further, in the step S1, after adding the rare earth magnetic powder to the weak acid solution, performing a first ultrasonic vibration, as to perform the weak acidification treatment; preferably, the power of the first ultrasonic vibration is 1500-2500 W, and the time length is 2-5 min.

[0009] Further, the phosphating solution is zinc-based phosphating solution or manganese-based phosphating solution; preferably, after the weak acidification treatment is completed, the phosphating solution is directly added to a system containing the weakly acidified magnetic powder, until a pH value of the system reaches 4-5, and then a second ultrasonic vibration is performed, as to perform the phosphating treatment; and preferably, the power of the second ultrasonic vibration is 1000-1500 W, and the time length is 10-15 min.

[0010] Further, the coupling agent is a silane coupling agent, preferably one or more of KH550, KH560, and KH792; preferably, after the phosphating treatment is completed, the coupling agent is directly added to a system containing the phosphating magnetic powder, and then a third ultrasonic vibration is performed, as to perform the coupling treatment; preferably, the added amount of the coupling agent is 0.5-1 % of the weight of the rare earth magnetic powder; preferably, the power of the third ultrasonic vibration is 1200-2000 W, and the time length is 10-15 min; and preferably, the drying process adopts vacuum drying, and the drying temperature is 70-90°C.

[0011] Further, the rare earth magnetic powder is one or more of isotropic neodymium iron boron magnetic powder, anisotropic neodymium iron boron magnetic powder, isotropic samarium iron nitrogen magnetic powder, anisotropic samarium iron nitrogen magnetic powder and samarium cobalt magnetic powder.

[0012] According to another aspect of the present disclosure, a preparation method for an injection molding rare earth magnetic material is further provided, and it includes the following steps: using the above surface treatment method to perform surface treatment on rare earth magnetic powder; and mixing the surface treated rare earth magnetic powder with a binder, and then extruding and granulating, to obtain the injection molding rare earth magnetic material.

[0013] Further, the binder is one or more of nylon, polyphenylene sulfide, and polyether ether ketone; preferably, the amount of the binder is 8-15% of the weight of the rare earth magnetic powder.

[0014] Further, the extruding and granulating process adopts a double-screw extruder, and the temperature of the extruding and granulating is 200-310°C.

[0015] According to another aspect of the present disclosure, an injection molding rare earth magnetic material is further provided, and it is prepared by the above preparation method.

[0016] The present disclosure provides a surface treatment method of rare earth magnetic powder, and it is to sequentially perform the weak acidification treatment, the phosphating treatment and the coupling treatment on the rare earth magnetic powder. The weak acidification treatment is the basis of the phosphating treatment and the coupling treatment, it may increase the number of the active sites on the surface of the rare earth magnetic powder, and may also dissolve insoluble ferrous iron and iron compound impurities on the surface of the rare earth magnetic powder, so that it is converted into a weak acid ferrous iron. The phosphating treatment and the coupling treatment are performed after the weak acidification treatment, and the more complete and higher-quality phosphating film and coupling protective layer may be formed on the surface of the rare earth magnetic powder, thereby the treated rare earth magnetic powder has the better oxidation resistance, the rare earth magnetic powder may be protected and prevented from being oxidized before and during the subsequent injection molding with the binder, and the obtained injection molding rare earth magnetic material has the better magnetic performance correspondingly.

Detailed Description of the Embodiments

[0017] It should be noted that embodiments in the present application and features in the embodiments may be combined with each other in the case without conflicting. The present disclosure is described in detail below in combination with the embodiments.

[0018] As described in the background, the rare earth magnetic powder in the existing technology has the weak oxidation resistance, so that the rare earth magnetic material after injection molding is poor in magnetic performance.

[0019] In order to solve this problem, the present disclosure provides a surface treatment method of rare earth magnetic powder, and it includes the following steps:

Step S1, adding rare earth magnetic powder to weak acid solution, as to weakly acidify the surface of the rare earth magnetic powder, to form weakly acidified magnetic powder, herein a weak acid in the weak acid solution is an inorganic weak acid with an acidity coefficient pKa value greater than 4.5 and/or an organic weak acid with an acidity

coefficient greater than 1.0.

Step S2, phosphating the weakly acidified magnetic powder with phosphating solution, to form phosphating magnetic powder.

Step S3, mixing the phosphating magnetic powder with a coupling agent, as to coupling-treat the phosphating magnetic powder, and then drying, to obtain a surface treated rare earth magnetic powder.

[0020] The present disclosure provides a surface treatment method of rare earth magnetic powder, and it is to sequentially perform the weak acidification treatment, the phosphating treatment and the coupling treatment on the rare earth magnetic powder. The weak acidification treatment is the basis of the phosphating treatment and the coupling treatment, it may increase the number of the active sites on the surface of the rare earth magnetic powder, and may also dissolve insoluble ferrous iron and iron compound impurities on the surface of the rare earth magnetic powder, so that it is converted into a weak acid ferrous iron. The increase in the number of the active sites may increase the number of sites on the surface of the rare earth magnetic powder that participate in a phosphating reaction and a coupling reaction, so that the degree of phosphating during the phosphating treatment may be improved, and the coupling treatment is also more adequate. The weak acid ferrous iron formed by the dissolution of impurities such as ferrous iron and iron compounds close to or remaining on the surface of the rare earth magnetic powder may act as a phosphating nucleus to a certain extent during the phosphating process, and it is also beneficial to the growth and formation of the phosphating film. The above two reasons are both helpful to improve the integrity and quality of the phosphating film, and the coupling protective layer is also more complete correspondingly. Therefore, the phosphating treatment and the coupling treatment are performed after the weak acidification treatment, and the more complete and higher-quality phosphating film and coupling protective layer may be formed on the surface of the rare earth magnetic powder, thereby the treated rare earth magnetic powder has the better oxidation resistance, the rare earth magnetic powder may be protected and prevented from being oxidized before and during the subsequent injection molding with the binder, and the obtained injection molding rare earth magnetic material has the better magnetic performance correspondingly.

[0021] In addition, compared to a mode of using a combination of the phosphating solution and coupling agent for treatment, the present disclosure sequentially performs the phosphating treatment and the coupling treatment after the weak acidification treatment, so that the growth of the phosphating film is more complete, and correspondingly the coupling protective layer is also more complete, it is further beneficial to the improvement of the oxidation resistance of the rare earth magnetic powder. At the same time, this operation is more beneficial to improve the compatibility and binding force of the rare earth magnetic powder with a polymer material during a later mixing and granulating process of the rare earth magnetic powder.

[0022] In a word, the surface treatment method provided by the present disclosure is used to treat the rare earth magnetic powder, it may significantly improve the oxidation resistance thereof, and correspondingly it is possible to prepare the high-performance and high-stability injection molding rare earth magnetic material.

[0023] The above weak acid adopts an inorganic weak acid with an acidity coefficient pKa value greater than 4.5 and/or an organic weak acid with an acidity coefficient greater than 1.0, it may increase the number of the active sites on the surface of the magnetic powder as much as possible on the basis without harming a body of the rare earth magnetic powder, in order to make the weak acidification treatment more effective, in a preferred embodiment, the weak acid adopts one or more of an oxalic acid, an acetic acid and a carbonic acid.

[0024] Preferably, a pH of the weak acid solution is 5-7. The pH value of the weak acid solution is controlled within the above range, it is beneficial to control the stability of the weak acidification treatment, and at the same time promotes the weak acidification treatment to be more adequate, so it has the further promotion effect on the growth quality and integrity of the subsequent phosphating film and coupling protective layer. In addition, in order to make the rare earth magnetic powder more fully dispersed and coated in the weak acid solution, preferably, ethanol may be used as a pH adjuster to adjust the pH value of the weak acid solution to 5-7. A specific solvent in the weak acid solution includes, but is not limited to, one or more of isopropanol, ethanol, and deionized water.

[0025] The added amount of the above weak acid solution should be sufficient to wrap the rare earth magnetic powder. In consideration of further improving the treatment effect, in a preferred embodiment, the volume ratio of the weak acid solution to the rare earth magnetic powder is 1.5-3:1.

[0026] As described above, the weak acidification treatment may also dissolve the ferrous iron and iron compound impurities on the surface of the rare earth magnetic powder, and convert it into the weak acid ferrous iron. These weak acid ferrous irons play a role of the phosphating nucleus to a certain extent in the phosphating process. In order to fully play this role, in a preferred embodiment, in the step S1, after the rare earth magnetic powder is added to the weak acid solution, first ultrasonic vibration is performed, as to perform the weak acidification treatment. Through the ultrasonic vibration, the weak acid ferrous irons may be more evenly distributed on the surface of the weakly acidified magnetic powder, thereby the growth of the phosphating film is more uniform and complete, and it is also helpful to improve the

efficiency of the phosphating treatment. At the same time, slight friction between the magnetic powder during the ultrasonic vibration process may also improve the morphology of the magnetic powder on a microscopic level, so that it is closer to a spherical shape, thereby the fluidity of a subsequent product is improved, the degree of orientation of the injection molding product is increased, and the magnetic performance of the injection molding rare earth magnetic material is further improved. Preferably, the power of the first ultrasonic vibration is 1500-2500 W, and the time length is 2-5 min. Under this power and time length, the above effects may be fully exerted. The preferred power is 2000 W.

[0027] In a preferred embodiment, the phosphating solution is zinc-based phosphating solution or manganese-based phosphating solution (available from Enthusiasm Company). The use of the above phosphating solution may perform more sufficient phosphating treatment on the weakly acidified magnetic powder, and the formed phosphating film is higher in quality, and is more complete and stable. More preferably, the zinc-based phosphating solution is used as the phosphating solution (such as Enthusiasm BW-231 special material zinc-manganese-based phosphating solution).

[0028] In order to make the phosphating treatment process more effective, in a preferred embodiment, after the weak acidification treatment is completed, the phosphating solution is directly added to a system containing the weakly acidified magnetic powder, until a pH value of the system reaches 4-5, and then, second ultrasonic vibration is performed, as to perform the phosphating treatment. In a specific implementation process, the second ultrasonic vibration treatment and the first ultrasonic vibration treatment are uninterrupted, so that the addition of the phosphating solution and the phosphating treatment may be performed under a condition of continuous vibration, and the effect is better. Preferably, the power of the second ultrasonic vibration is 1000-1500 W, and the time length is 10-15 min, more preferably the power is 1500 W.

[0029] The above coupling agent may adopt a commonly used type in the field, and preferably, the coupling agent is a silane coupling agent. The use of the silane coupling agent may form the better coupling protective film on the surface of the phosphating magnetic powder, and it may further improve the fusion between the magnetic powder and the binder during the subsequent injection molding granulating process with the binder, so that the material distribution is more uniform, and the magnetic performance of the final material is better. More preferably, the coupling agent is one or more of KH550, KH560, and KH792.

[0030] In order to make the coupling treatment effect better, in a preferred embodiment, after the phosphating treatment is completed, the coupling agent is directly added to a system containing the phosphating magnetic powder, and then third ultrasonic vibration is performed, as to perform the coupling treatment. In a specific implementation process, the third ultrasonic vibration and the second ultrasonic vibration are uninterrupted, so that the coupling treatment may be performed under a state of continuous vibration, and the coupling protective layer formed is more uniform and complete. Preferably, the added amount of the coupling agent is 0.5-1 % of the weight of the rare earth magnetic powder. The amount of the coupling agent is controlled within the above range, so that it may be fully distributed on the surface of the phosphating magnetic powder, it is more beneficial to improve the oxidation resistance of the magnetic powder and the compatibility between the magnetic powder and the binder during the injection molding process, so that the final material obtained by the granulation has the better magnetic performance and stability. Preferably, the power of the third ultrasonic vibration is 1200-2000 W, and the time length is 10-15 min; and the preferred power is 1500 W. Preferably, the drying process adopts vacuum drying, and the drying temperature is 70-90°C.

[0031] The above surface treatment method of the present disclosure is suitable for many types of rare earth magnetic powder, including but not limited to the rare earth magnetic powder which is one or more of isotropic neodymium iron boron magnetic powder (Nd-Fe-B), anisotropic neodymium iron boron magnetic powder (Nd-Fe-B), isotropic samarium iron nitrogen magnetic powder (Sm-Fe-N), anisotropic samarium iron nitrogen magnetic powder (Sm-Fe-N) and samarium cobalt magnetic powder (Sm-Co).

[0032] According to another aspect of the present disclosure, a preparation method for an injection molding rare earth magnetic material is further provided, and it includes the following steps: using the above surface treatment method to perform surface treatment on rare earth magnetic powder; and mixing the surface treated rare earth magnetic powder with a binder, and then extruding and granulating, to obtain the injection molding rare earth magnetic material. The surface treatment method provided by the present disclosure is used to treat the rare earth magnetic powder, the oxidation resistance thereof may be significantly improved, and the rare earth magnetic powder may be protected and prevented from being oxidized before and during the subsequent injection molding with the binder, and correspondingly the high-performance high-stability injection molding rare earth magnetic material may be prepared.

[0033] The above binder may be nylon, such as nylon 6, nylon 12, nylon 11, and nylon 66, or it may be polyphenylene sulfide (PPS) with the better temperature resistance, or polyether ether ketone (PEEK) and other materials. These materials may be used by one or a combination of them. Preferably, the amount of the binder is 8-15% of the weight of the rare earth magnetic powder.

[0034] In a preferred embodiment, the extruding and granulating process adopts a double-screw extruder, and the temperature of the extruding and granulating is 200-310°C.

[0035] According to another aspect of the present disclosure, an injection molding rare earth magnetic material is further provided, and it is prepared by the above preparation method.

[0036] Benefited from the good oxidation resistance of the rare earth magnetic powder after the surface treatment, the injection molding rare earth magnetic material has the more excellent magnetic performance and stability.

[0037] The beneficial effects of the present disclosure are further described in detail below in combination with the specific embodiments:

Embodiment 1

[0038] Various raw materials and weight parts of the raw materials in this embodiment are as follows.

Rare earth magnetic powder: isotropic NdFeB magnetic powder (15-9 magnetic powder from Magnequench Company, 92 parts by weight).

Coupling agent: silane coupling agent (KH550, 0.5 parts by weight).

Binder: nylon 12 powder (nylon from Ube, Japan, 7.5 parts by weight).

[0039] The process steps are as follows.

[0040] 0.01 mol/L of oxalic acid isopropanol solution is dissolved in absolute ethanol, a pH value is adjusted to 5, to form weak acid solution; rare earth magnetic powder is added to it, the weak acid solution may completely wrap the magnetic powder, and its volume ratio to the magnetic powder is 1.5:1; ultrasonic vibration is turned on, the power is controlled to 2000 W, and it is treated for 5 min, to form a system containing the weakly acidified magnetic powder.

[0041] BW-231 zinc-based phosphating solution of Enthusiasm Company is added to the above system, the added amount is based on the pH value, the pH value is adjusted to 4, the ultrasonic vibration is continuously performed, the power is controlled to 1500 W, and the treatment time is 15 min, to form a system containing the phosphating magnetic powder.

[0042] The coupling agent is continuously added to the system, the ultrasonic vibration is performed, and the power is controlled to 1500 W, after 10 min, the system is vacuum-dried at 80°C for 5 h, to obtain the rare earth magnetic powder after the surface treatment.

[0043] The rare earth magnetic powder after the surface treatment is mixed with the binder and granulated by using a double-screw extruder, and the granulating temperature is set at 200-220°C, to obtain the high-performance injection molding rare earth magnetic material.

[0044] According to relevant test standards of IEC 60404-8-1, the performance of an injection molding rare earth magnetic material sample is tested, and results are as follows: Br=0.58T, Hcj=737KA/m, (BH)m=52KJ/m³, and the melt index is 306 g/ 10 min.

Embodiment 2

[0045] Various raw materials and weight parts of the raw materials in this embodiment are as follows.

Rare earth magnetic powder: isotropic NdFeB magnetic powder (15-9 magnetic powder from Magnequench Company, 90 parts by weight).

Coupling agent: silane coupling agent (KH550, 0.5 parts by weight).

Binder: PPS powder (Tosoh 100#, Japan, 9.5 parts by weight).

[0046] The process steps are as follows.

[0047] 0.01 mol/L of oxalic acid isopropanol solution is dissolved in absolute ethanol, a pH value is adjusted to 7, to form weak acid solution; rare earth magnetic powder is added to it, the weak acid solution may completely wrap the magnetic powder, and its volume ratio to the magnetic powder is 2:1; ultrasonic vibration is turned on, the power is controlled to 2000 W, and it is treated for 5 min, to form a system containing the weakly acidified magnetic powder.

[0048] BW-231 zinc-based phosphating solution of Enthusiasm Company is added to the above system, the added amount is based on the pH value, the pH value is adjusted to 5, the ultrasonic vibration is continuously performed, the power is controlled to 1500 W, and the treatment time is 15 min, to form a system containing the phosphating magnetic powder.

[0049] The coupling agent is continuously added to the system, the ultrasonic vibration is performed, and the power is controlled to 1500 W, after 10 min, the system is vacuum-dried at 80°C for 5 h, to obtain the rare earth magnetic powder after the surface treatment.

[0050] The rare earth magnetic powder after the surface treatment is mixed with the binder and granulated by using a double-screw extruder, and the granulating temperature is set at 290-310°C, to obtain the high-performance injection molding rare earth magnetic material.

[0051] According to relevant test standards of IEC 60404-8-1, the performance of an injection molding rare earth magnetic material sample is tested, and results are as follows: Br=0.54T, Hcj=709KA/m, (BH)m=49KJ/m³, and the melt index is 183 g/10 min.

Embodiment 3

[0052] Various raw materials and weight parts of the raw materials in this embodiment are as follows.

Rare earth magnetic powder: anisotropic Sm₂F₁₇Nx magnetic powder (D₅₀ is 2.5μm, 91 parts by weight).

Coupling agent: silane coupling agent (KH550, 0.5 parts by weight).

Binder: nylon 12 powder (nylon from Ube, Japan, 8.5 parts by weight).

[0053] The process steps are as follows.

[0054] 0.01 mol/L of oxalic acid isopropanol solution is dissolved in absolute ethanol, a pH value is adjusted to 7, to form weak acid solution; rare earth magnetic powder is added to it, the weak acid solution may completely wrap the magnetic powder, and its volume ratio to the magnetic powder is 3:1; ultrasonic vibration is turned on, the power is controlled to 2000 W, and it is treated for 5 min, to form a system containing the weakly acidified magnetic powder.

[0055] BW-231 zinc-based phosphating solution of Enthusiasm Company is added to the above system, the added amount is based on the pH value, the pH value is adjusted to 5, the ultrasonic vibration is continuously performed, the power is controlled to 1500 W, and the treatment time is 15 min, to form a system containing the phosphating magnetic powder.

[0056] The coupling agent is continuously added to the system, the ultrasonic vibration is performed, and the power is controlled to 1500 W, after 10 min, the system is vacuum-dried at 80°C for 5 h, to obtain the rare earth magnetic powder after the surface treatment.

[0057] The rare earth magnetic powder after the surface treatment is mixed with the binder and granulated by using a double-screw extruder, and the granulating temperature is set at 200-220°C, to obtain the high-performance injection molding rare earth magnetic material.

[0058] According to relevant test standards of IEC 60404-8-1, the performance of an injection molding rare earth magnetic material sample is tested, and results are as follows: Br=0.64T, Hcj=725KA/m, (BH)m=65KJ/m³, and the melt index is 142 g/10 min.

Embodiment 4

[0059] Various raw materials and weight parts of the raw materials in this embodiment are as follows.

Rare earth magnetic powder: anisotropic Sm₂F₁₇Nx magnetic powder (D₅₀ is 2.5μm, 89 parts by weight).

Coupling agent: silane coupling agent (KH550, 0.5 parts by weight).

Binder: PPS powder (Tosoh 100#, Japan, 10.5 parts by weight).

[0060] The process steps are as follows.

[0061] 0.01 mol/L of oxalic acid isopropanol solution is dissolved in absolute ethanol, a pH value is adjusted to 6, to form weak acid solution; rare earth magnetic powder is added to it, the weak acid solution may completely wrap the magnetic powder, and its volume ratio to the magnetic powder is 1.5:1; ultrasonic vibration is turned on, the power is controlled to 2000 W, and it is treated for 5 min, to form a system containing the weakly acidified magnetic powder.

[0062] BW-231 zinc-based phosphating solution of Enthusiasm Company is added to the above system, the added amount is based on the pH value, the pH value is adjusted to 5, the ultrasonic vibration is continuously performed, the power is controlled to 1500 W, and the treatment time is 15 min, to form a system containing the phosphating magnetic powder.

[0063] The coupling agent is continuously added to the system, the ultrasonic vibration is performed, and the power is controlled to 1500 W, after 10 min, the system is vacuum-dried at 80°C for 5 h, to obtain the rare earth magnetic powder after the surface treatment.

[0064] The rare earth magnetic powder after the surface treatment is mixed with the binder and granulated by using a double-screw extruder, and the granulating temperature is set at 290-310°C, to obtain the high-performance injection molding rare earth magnetic material.

[0065] According to relevant test standards of IEC 60404-8-1, the performance of an injection molding rare earth magnetic material sample is tested, and results are as follows: Br=0.59T, Hcj=695KA/m, (BH)m=59KJ/m³, and the melt index is 108 g/ 10 min.

Embodiment 5

[0066] A different from Embodiment 1 is only that the weak acid is an acetic acid, and the silane coupling agent is KH560. According to relevant test standards of IEC 60404-8-1, the performance of an injection molding rare earth magnetic material sample is tested, and results are as follows: Br=0.58 T, Hcj=726 KA/m, (BH)m=52 KJ/m³, and the melt index is 312 g/10 min.

Embodiment 6

[0067] A different from Embodiment 1 is only that the weak acid is a carbonic acid, and the silane coupling agent is KH792. According to relevant test standards of IEC 60404-8-1, the performance of an injection molding rare earth magnetic material sample is tested, and results are as follows: Br=0.59 T, Hcj=724 KA/m, (BH)m=53 KJ/m³, and the melt index is 300 g /10 min.

Embodiment 7

[0068] A different from Embodiment 1 is only that:

Ethanol is used to adjust a pH value of weak acid solution to 7, and the volume ratio of the weak acid solution to the rare earth magnetic powder is 3:1; the power of the first ultrasonic vibration is 1500 W, and it is treated for 2 min.

[0069] Zinc-based phosphating solution is added to a system containing weakly acidified magnetic powder, the pH value is adjusted to 5, the ultrasonic vibration is continuously performed, the power is controlled to 1000 W, and the treatment time is 10 min, to form a system containing the phosphating magnetic powder.

[0070] A coupling agent is continuously added to the system, the added amount of the coupling agent is 0.5% of the weight of the rare earth magnetic powder, the ultrasonic vibration is performed, and the power is controlled to 2000 W, after 15 min, the system is vacuum-dried at 90°C for 5 h, to obtain the rare earth magnetic powder after the surface treatment.

[0071] According to relevant test standards of IEC 60404-8-1, the performance of an injection molding rare earth magnetic material sample is tested, and results are as follows: Br=0.59T, Hcj=753 KA/m, (BH)m=53 KJ/m³, and the melt index is 275 g/10 min.

Embodiment 8

[0072] A different from Embodiment 1 is only that:

Ethanol is used to adjust a pH value of weak acid solution to 6, and the volume ratio of the weak acid solution to the rare earth magnetic powder is 2:1; the power of the first ultrasonic vibration is 2500 W, and it is treated for 4 min.

[0073] Zinc-based phosphating solution is added to a system containing weakly acidified magnetic powder, the pH value is adjusted to 5, the ultrasonic vibration is continuously performed, the power is controlled to 1500 W, and the treatment time is 15 min, to form a system containing the phosphating magnetic powder.

[0074] A coupling agent is continuously added to the system, the added amount of the coupling agent is 1% of the weight of the rare earth magnetic powder, the ultrasonic vibration is performed, and the power is controlled to 1200 W, after 15 min, the system is vacuum-dried at 90°C for 7 h, to obtain the rare earth magnetic powder after the surface treatment.

[0075] According to relevant test standards of IEC 60404-8-1, the performance of an injection molding rare earth magnetic material sample is tested, and results are as follows: Br=0.58T, Hcj=706 KA/m, (BH)m=51 KJ/m³, and the melt index is 328 g/10 min.

Contrast example 1

[0076] Various raw materials and weight parts of the raw materials in this contrast example are as follows.

Rare earth magnetic powder: isotropic NdFeB magnetic powder (15-9 magnetic powder from Magnequench Com-

pany, 92 parts).

Coupling agent: silane coupling agent (KH550, 0.5 parts).

5 Phosphoric acid: 0.5 parts.

Binder: nylon 12 powder (nylon from Ube, Japan, 7 parts).

[0077] The process steps are as follows.

10 **[0078]** The silane coupling agent and the phosphoric acid are dissolved in an appropriate amount of anhydrous ethanol, the rare earth magnetic powder is added to it, the amount of the anhydrous ethanol is enough to completely wrap the magnetic powder, and its volume ratio to the magnetic powder is 1.5:1; and then the rare earth magnetic powder is added to the solution, it is fully stirred and mixed uniformly, and then vacuum-dried at 80°C for 5 h, to obtain the rare earth magnetic powder after the surface treatment.

15 **[0079]** The rare earth magnetic powder after the surface treatment is mixed with the binder and granulated by using a double-screw extruder, and the granulating temperature is set at 200-220°C, to obtain the injection molding rare earth magnetic material.

[0080] According to relevant test standards, the performance of an injection molding rare earth magnetic material sample is tested, and results are as follows: Br=0.56T, Hcj=716 KA/m, (BH)m=48 KJ/m³, and the melt index is 264 g/10 min.

Contrast example 2

[0081] Various raw materials and weight parts of the raw materials in this contrast example are as follows.

25 Rare earth magnetic powder: isotropic NdFeB magnetic powder (15-9 magnetic powder from Magnequench Company, 90 parts).

30 Coupling agent: silane coupling agent (KH550, 0.5 parts).

Phosphoric acid: 0.5 parts.

Binder: PPS powder (Tosoh 100#, Japan, 9 parts).

35 **[0082]** The process steps are as follows.

[0083] The silane coupling agent and the phosphoric acid are dissolved in an appropriate amount of anhydrous ethanol, the rare earth magnetic powder is added to it, the amount of the anhydrous ethanol is enough to completely wrap the magnetic powder, and its volume ratio to the magnetic powder is 2:1; and then the rare earth magnetic powder is added to the solution, it is fully stirred and mixed uniformly, and then vacuum-dried at 80°C for 5 h, to obtain the rare earth magnetic powder after the surface treatment.

40 **[0084]** The rare earth magnetic powder after the surface treatment is mixed with the binder and granulated by using a double-screw extruder, and the granulating temperature is set at 290-310°C, to obtain the injection molding rare earth magnetic material.

[0085] According to relevant test standards, the performance of an injection molding rare earth magnetic material sample is tested, and results are as follows: Br=0.51T, Hcj=674 KA/m, (BH)m=46 KJ/m³, and the melt index is 152 g/10 min.

Contrast example 3

50 **[0086]** Various raw materials and weight parts of the raw materials in this contrast example are as follows.

Rare earth magnetic powder: anisotropic Sm₂F₁₇Nx magnetic powder (D₅₀ is 2.5μm, 91 parts).

55 Coupling agent: silane coupling agent (KH550, 0.5 parts).

Phosphoric acid: 0.5 parts.

Binder: nylon 12 powder (nylon from Ube, Japan, 8 parts).

[0087] The process steps are as follows.

[0088] The silane coupling agent and the phosphoric acid are dissolved in an appropriate amount of anhydrous ethanol, the rare earth magnetic powder is added to it, the amount of the anhydrous ethanol is enough to completely wrap the magnetic powder, and its volume ratio to the magnetic powder is 3:1; and then the rare earth magnetic powder is added to the solution, it is fully stirred and mixed uniformly, and then vacuum-dried at 80°C for 5 h, to obtain the rare earth magnetic powder after the surface treatment.

[0089] The rare earth magnetic powder after the surface treatment is mixed with the binder and granulated by using a double-screw extruder, and the granulating temperature is set at 200-220°C, to obtain the injection molding rare earth magnetic material.

[0090] According to relevant test standards, the performance of an injection molding rare earth magnetic material sample is tested, and results are as follows: Br=0.58T, Hcj=684 KA/m, (BH)m=59 KJ/m³, and the melt index is 138 g/10 min.

Contrast example 4

[0091] Various raw materials and weight parts of the raw materials in this contrast example are as follows.

Rare earth magnetic powder: anisotropic Sm₂F₁₇Nx magnetic powder (D₅₀ is 2.5μm, 89 parts).

Binder: PPS powder (Tosoh 100#, Japan, 10.5 parts).

Coupling agent: silane coupling agent (KH550, 0.5 parts).

[0092] The process steps are as follows.

[0093] The silane coupling agent and the phosphoric acid are dissolved in an appropriate amount of anhydrous ethanol, the rare earth magnetic powder is added to it, the amount of the anhydrous ethanol is enough to completely wrap the magnetic powder, and its volume ratio to the magnetic powder is 1.5:1; and then the rare earth magnetic powder is added to the solution, it is fully stirred and mixed uniformly, and then vacuum-dried at 80°C for 5 h, to obtain the rare earth magnetic powder after the surface treatment.

[0094] The rare earth magnetic powder after the surface treatment is mixed with the binder and granulated by using a double-screw extruder, and the granulating temperature is set at 290-310°C, to obtain the injection molding rare earth magnetic material.

[0095] According to relevant test standards, the performance of an injection molding rare earth magnetic material sample is tested, and results are as follows: Br=0.52T, Hcj=625 KA/m, (BH)m=52 KJ/m³, and the melt index is 117 g/10 min.

Table 1

		Embodiment 1	Embodiment 2	Embodiment 3	Embodiment 4	Contrast example 1	Contrast example 2	Contrast example 3	Contrast example 4
Br	T	0.58	0.54	0.64	0.59	0.56	0.51	0.58	0.52
Hcj	KA/m	737	709	725	695	716	674	684	625
(BH) max	KJ/m ³	52	49	65	59	48	46	59	52
Fluidity	g/10min	306	183	142	108	264	152	138	117
		Embodiment 5	Embodiment 6	Embodiment 7	Embodiment 8				
Br	T	0.58	0.59	0.59	0.58				
Hcj	KA/m	726	724	753	706				
(BH) max	KJ/m ³	52	53	53	51				
Fluidity	g/10min	312	300	275	328				

[0096] Br, H_{cj}, and (BH) max are all important indicators of the magnetic performance of the permanent magnet material. After the rare earth permanent magnet material is oxidized, the performance is decreased, and these indicators may be decreased accordingly. The oxidation is more severe, and these indicators are decreased more. It may be seen from the above table that the Br, H_{cj}, and (BH) max indicators of the injection molding rare earth magnetic material prepared by using the rare earth magnetic powder treated by the surface treatment method in the embodiment of the present disclosure are significantly improved, it is indicated that the oxidation resistance thereof is stronger, and the magnetic performance of the injection molding rare earth magnetic material is better. It should be noted that for the different binders, there is a big difference in temperature during the injection molding, and the preparation of the magnetic powder at different temperatures may bring about a larger difference. Therefore, the differences between the performances of the rare earth magnetic powder injection molding materials prepared in the above Embodiments 1 to 4 are significant. However, it is respectively compared with Contrast examples 1 to 4, the performance of the injection molding material corresponding to the same binder or the same magnetic powder is significantly improved, and it is sufficient to indicate the beneficial effects brought by the surface treatment method of the present disclosure.

[0097] Fluidity refers to a melt flow rate of a finished product under a certain pressure and a certain molten state. Magnetic powder agglomeration or irregular morphology of the magnetic powder may affect the fluidity. It may be seen from the above table that the melt index of the injection molding rare earth magnetic material prepared by using the surface treatment method in the embodiment of the present disclosure is significantly improved, and it is indicated that the rare earth magnetic powder has the more regular morphology, and the compatibility with the binder after the surface treatment is better.

[0098] The above are only preferred embodiments of the present disclosure, and are not used to limit the present disclosure. For those skilled in the art, the present disclosure may have various modifications and changes. Any modifications, equivalent replacements, improvements and the like made within the spirit and principle of the present disclosure should be included in a scope of protection the present disclosure.

Claims

1. A surface treatment method of rare earth magnetic powder, comprising the following steps:

step S1, adding rare earth magnetic powder to weak acid solution, as to weakly acidify the surface of the rare earth magnetic powder, to form weakly acidified magnetic powder; wherein, a weak acid in the weak acid solution is an inorganic weak acid with an acidity coefficient pK_a value greater than 4.5 and/or an organic weak acid with an acidity coefficient greater than 1.0;

step S2, phosphating the weakly acidified magnetic powder with phosphating solution, to form phosphating magnetic powder; and

step S3, mixing the phosphating magnetic powder with a coupling agent, as to coupling-treat the phosphating magnetic powder, and then drying, to obtain a surface treated rare earth magnetic powder.

2. The surface treatment method according to claim 1, wherein the weak acid is one or more of an oxalic acid, an acetic acid and a carbonic acid;

preferably, a pH value of the weak acid solution is 5-7;

preferably, ethanol is used to adjust the pH value of the weak acid solution; and

preferably, a volume ratio of the weak acid solution to the rare earth magnetic powder is 1.5-3:1.

3. The surface treatment method according to claim 1 or 2, wherein in the step S1, after adding the rare earth magnetic powder to the weak acid solution, performing a first ultrasonic vibration, as to perform the weak acidification treatment; preferably, the power of the first ultrasonic vibration is 1500-2500 W, and the time length is 2-5 min.

4. The surface treatment method according to any one of claims 1 to 3, wherein the phosphating solution is zinc-based phosphating solution or manganese-based phosphating solution;

preferably, after the weak acidification treatment is completed, the phosphating solution is directly added to a system containing the weakly acidified magnetic powder, until a pH value of the system reaches 4-5, and then a second ultrasonic vibration is performed, as to perform the phosphating treatment; and preferably, the power of the second ultrasonic vibration is 1000-1500 W, and the time length is 10-15 min.

5. The surface treatment method according to claim 4, wherein the coupling agent is a silane coupling agent, preferably

one or more of KH550, KH560, and KH792;

preferably, after the phosphating treatment is completed, the coupling agent is directly added to a system containing the phosphating magnetic powder, and then a third ultrasonic vibration is performed, as to perform the coupling treatment;

preferably, the added amount of the coupling agent is 0.5-1% of the weight of the rare earth magnetic powder; preferably, the power of the third ultrasonic vibration is 1200-2000 W, and the time length is 10-15 min; and preferably, the drying process adopts vacuum drying, and the drying temperature is 70-90°C.

6. The surface treatment method according to any one of claims 1 to 3, wherein the rare earth magnetic powder is one or more of isotropic neodymium iron boron magnetic powder, anisotropic neodymium iron boron magnetic powder, isotropic samarium iron nitrogen magnetic powder, anisotropic samarium iron nitrogen magnetic powder and samarium cobalt magnetic powder.

7. A preparation method for an injection molding rare earth magnetic material, comprising the following steps:

using the surface treatment method according to any one of claims 1 to 6 to perform surface treatment on rare earth magnetic powder; and

mixing the surface treated rare earth magnetic powder with a binder, and then extruding and granulating, to obtain the injection molding rare earth magnetic material.

8. The preparation method according to claim 7, wherein the binder is one or more of nylon, polyphenylene sulfide, and polyether ether ketone; preferably, the amount of the binder is 8-15% of the weight of the rare earth magnetic powder.

9. The preparation method according to claim 7, wherein the extruding and granulating process adopts a double-screw extruder, and the temperature of the extruding and granulating is 200-310°C.

10. An injection molding rare earth magnetic material, wherein it is prepared by the preparation method according to any one of claims 7 to 9.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2021/129091

A. CLASSIFICATION OF SUBJECT MATTER H01F 41/02(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) H01F 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) CNTXT, DWPI, SIPOABS, ENTXT, Elsevier Science Direct, ISI Web of Science, 读秀, DUXIU, 超星科技数字图书馆, CHAOXING, 中国期刊网全文数据库, CJFD: 横店集团东磁股份有限公司, 磁粉, 表面, 弱酸, 磷化, 偶联剂, 超声, 注塑, 挤压, magnet, surface, acid, phosphat+, coupling, ultrasound, inject+, extru+																					
C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>Y</td> <td>CN 107603220 A (HENGDIAN GROUP DMEGC MAGNETICS CO., LTD.) 19 January 2018 (2018-01-19) description, paragraphs 0005-0016</td> <td>1-10</td> </tr> <tr> <td>Y</td> <td>US 5013411 A (SHINETSU CHEMICAL CO., LTD.) 07 May 1991 (1991-05-07) description, column 3, line 20 to column 4, line 21</td> <td>1-10</td> </tr> <tr> <td>Y</td> <td>CN 102605361 A (BEIJING ZHONG KE SAN HUAN HI-TECH CO., LTD.) 25 July 2012 (2012-07-25) claim 1</td> <td>1-10</td> </tr> <tr> <td>A</td> <td>CN 1808648 A (UNIVERSITY OF SCIENCE AND TECHNOLOGY BEIJING) 26 July 2006 (2006-07-26) entire document</td> <td>1-10</td> </tr> <tr> <td>A</td> <td>CN 106349686 A (CHE SHENGLEI et al.) 25 January 2017 (2017-01-25) entire document</td> <td>1-10</td> </tr> <tr> <td>A</td> <td>JP 2002008911 A (NICHIA KAGAKU KOGYO K.K.) 11 January 2002 (2002-01-11) entire document</td> <td>1-10</td> </tr> </tbody> </table>	Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	Y	CN 107603220 A (HENGDIAN GROUP DMEGC MAGNETICS CO., LTD.) 19 January 2018 (2018-01-19) description, paragraphs 0005-0016	1-10	Y	US 5013411 A (SHINETSU CHEMICAL CO., LTD.) 07 May 1991 (1991-05-07) description, column 3, line 20 to column 4, line 21	1-10	Y	CN 102605361 A (BEIJING ZHONG KE SAN HUAN HI-TECH CO., LTD.) 25 July 2012 (2012-07-25) claim 1	1-10	A	CN 1808648 A (UNIVERSITY OF SCIENCE AND TECHNOLOGY BEIJING) 26 July 2006 (2006-07-26) entire document	1-10	A	CN 106349686 A (CHE SHENGLEI et al.) 25 January 2017 (2017-01-25) entire document	1-10	A	JP 2002008911 A (NICHIA KAGAKU KOGYO K.K.) 11 January 2002 (2002-01-11) entire document	1-10
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Date of the actual completion of the international search 06 July 2022	Date of mailing of the international search report 27 July 2022																				
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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.
A	JP 2003142308 A (SUMITOMO METAL MINING CO.) 16 May 2003 (2003-05-16) entire document	1-10

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Information on patent family members

International application No.

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