



(11)

EP 4 570 948 A1

(12)

EUROPEAN PATENT APPLICATION
published in accordance with Art. 153(4) EPC

(43) Date of publication:

18.06.2025 Bulletin 2025/25

(51) International Patent Classification (IPC):

C23C 22/80 ^(2006.01) **C23C 22/60** ^(2006.01)
H01F 41/02 ^(2006.01)

(21) Application number: **23881143.4**

(86) International application number:

PCT/CN2023/090163

(22) Date of filing: **23.04.2023**

(87) International publication number:

WO 2024/087548 (02.05.2024 Gazette 2024/18)

(84) Designated Contracting States:

**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC ME MK MT NL
NO PL PT RO RS SE SI SK SM TR**

Designated Extension States:

BA

Designated Validation States:

KH MA MD TN

(72) Inventors:

- **ZHANG, Yanyan**
Longyan, Fujian 366300 (CN)
- **LIANG, Yamin**
Longyan, Fujian 366300 (CN)
- **FU, Donghui**
Longyan, Fujian 366300 (CN)
- **LAI, Huoxiu**
Longyan, Fujian 366300 (CN)
- **HUANG, Jiaying**
Longyan, Fujian 366300 (CN)

(30) Priority: **25.10.2022 CN 202211309391**

(71) Applicant: **FUJIAN GOLDEN DRAGON RARE-EARTH Co., Ltd.**
Fujian 366300 (CN)

(74) Representative: **Kuttenkeuler, David**
SKM-IP PartGmbH
Oberanger 45
80331 München (DE)

(54) **SURFACE TREATMENT METHOD FOR PERMANENT MAGNET, PERMANENT MAGNET AND PROTECTIVE FILM THEREOF**

(57) The present invention discloses a surface treatment method for a permanent magnet, a permanent magnet and a protective film thereof. The surface treatment method for the permanent magnet comprises the following steps of: S1: subjecting the permanent magnet to zirconization treatment to obtain a permanent magnet having a zirconization film, wherein the zirconization treatment is performed at a temperature of 5-40°C for a time of 5-30 min at a pH value of 1.5-6; and S2: subjecting the permanent magnet having the zirconiza-

tion film to passivation treatment followed by baking, wherein the passivation treatment is performed at a temperature of 15-50°C for a time of 4-12 min at a pH value of greater than or equal to 10. According to the treatment method of the present invention, the obtained permanent magnet has relatively good moisture resistance and relatively large surface tension; and the treatment method of the present invention reduces pollutant emission and conforms to the concept of green ecological and environmentally friendly production.

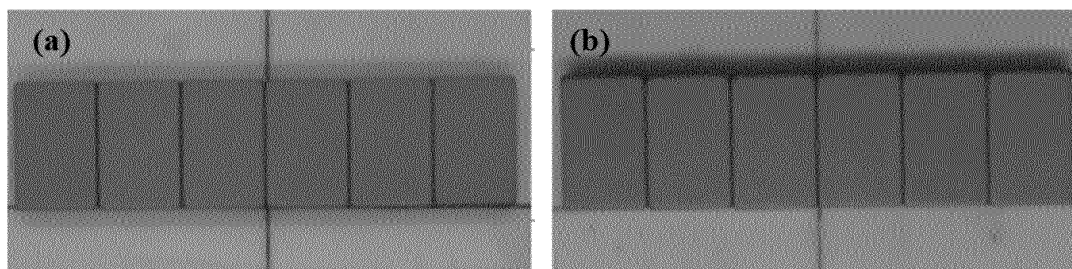


Fig. 1

EP 4 570 948 A1

Description**FIELD OF THE INVENTION**

- 5 **[0001]** The invention relates to a surface treatment method for a permanent magnet, a permanent magnet and a protective film thereof.

BACKGROUND OF THE INVENTION

- 10 **[0002]** Permanent magnet material is a porous material prepared by powder metallurgy process. The neodymium-rich phase, neodymium-iron-boron main phase and boundary phase are prone to inter-granular corrosion. The failure of magnets in humid air is mainly caused by oxidation and fracture of crystal particles, which eventually leads to the decline or damage of the magnetic properties of the material. This seriously affects the service life of permanent magnets and reduces the stability and reliability of the product.

- 15 **[0003]** With the continuous improvement of energy conservation, environmental protection and sewage discharge requirements in China and abroad, the traditional coating ternary phosphating pretreatment materials are gradually banned by local regulations because they contain pollutants such as P, Mn, and Ni. The new green phosphorus-free conversion film technology has gradually matured and developed rapidly. This process can completely avoid the use of harmful substances such as P, Mn, Ni, and nitrite. However, the coating surface obtained by the existing zirconium salt pretreatment process is uneven and has low corrosion resistance. In addition, after high temperature and high pressure test, wet heat test and neutral salt spray test, its anti-corrosion effect is poor.

- 20 **[0004]** In addition, in automotive applications, magnets need to be adhered and assembled with other workpieces by using an adhesive. For this reason, this type of application has higher requirements for the adhesiveness of the surface protective film of the magnet. For example, in car audio systems, it is necessary that the surface tension of the magnet should be 38 mN/m or higher so as to meet the adhesive requirements during assembly. However, although the conventional organic coatings have a certain degree of moisture resistance, their surface energy is low, which makes it difficult for the surface tension of the coating to reach a high level.

- 25 **[0005]** Therefore, when preparing a protective film on the surface of neodymium-iron-boron, it is necessary not only to consider that the protective film has better protection in conventional environments and high temperature-high humidity environments, that is, good moisture resistance, but also good surface tension to meet the requirements of subsequent processing.

SUMMARY OF THE INVENTION

- 35 **[0006]** In order to overcome the defects of the existing technology that permanent magnet materials are difficult to have good moisture resistance and surface tension at the same time, and the preparation process has large pollution, the present invention provides a surface treatment method for a permanent magnet, a permanent magnet and a protective film thereof. According to the treatment method of the present invention, the obtained permanent magnet has relatively good moisture resistance and relatively large surface tension; and the treatment method of the present invention reduces pollutant emission and conforms to the concept of green ecological and environmentally friendly production.

40 **[0007]** The present invention solves the above technical problems through the following technical solutions.

[0008] The present invention provides a surface treatment method for a permanent magnet, comprising the following steps of:

- 45 S1: subjecting the permanent magnet to zirconization treatment to obtain a permanent magnet having a zirconization film, wherein the zirconization treatment is performed at a temperature of 5-40°C for a time of 5-30 min at a pH value of 1.5-6; and

- S2: subjecting the permanent magnet having the zirconization film to passivation treatment followed by baking, wherein the passivation treatment is performed at a temperature of 15-50°C for a time of 4-12 min at a pH value of greater than or equal to 10.

[0009] In S1, preferably, the zirconization treatment is performed by immersing the permanent magnet in an aqueous solution comprising a zirconizing agent.

- 55 **[0010]** Wherein, the zirconizing agent may be a conventional zirconizing agent in the art; preferably, the zirconizing agent comprises fluorozirconate and/or fluorozirconic acid; more preferably, the zirconizing agent is a special zirconizing agent for rare earth neodymium-iron-boron materials, which comes from Hainan Hongxiang Industrial Co., Ltd.

[0011] Wherein, preferably, the aqueous solution comprising the zirconizing agent has a concentration of 10%-60%, wherein the concentration of the aqueous solution comprising the zirconizing agent is calculated by a mass percentage of

the zirconizing agent in the aqueous solution comprising the zirconizing agent.

[0012] Wherein, the immersing is direct immersing or indirect immersing. The direct immersing refers to immersing the permanent magnet in the aqueous solution containing the zirconizing agent. The indirect immersing is preferably drum immersing. The drum immersing refers to placing the permanent magnet in a drum and then immersing it in the aqueous solution comprising the zirconizing agent, and rotating the drum during the treatment process so that all surfaces of the permanent magnet are fully in contact with the zirconizing agent.

[0013] In S1, preferably, the zirconization treatment is performed at a temperature of 20-30°C.

[0014] In S1, preferably, the zirconization treatment is performed for a time of 10-25min, more preferably 15 min-20 min.

[0015] In S1, the adhesion effect of the zirconization film on the permanent magnet is related to the concentration of the aqueous solution comprising the zirconization agent; the pH value, temperature, and time for the zirconization treatment; and the surface cleanliness of the permanent magnet.

[0016] In S1, preferably, before the passivation treatment, the permanent magnet having the zirconization film is successively subjected to a third water washing and drying.

[0017] Wherein, preferably, the third water washing is performed for a time of 10-20 seconds.

[0018] Wherein, preferably, the third water washing has an overflow water flow of 100 cubic meters/hour.

[0019] Wherein, preferably, the drying is performed at a temperature of 80°C.

[0020] Wherein, preferably, the drying is performed for a time of 30min.

[0021] In S2, the passivation treatment is physical passivation. Compared with other passivation processes, the passivation treatment of the present invention can be carried out at a lower temperature.

[0022] In S2, preferably, the passivation treatment is performed in an aqueous solution comprising a passivating agent.

[0023] Wherein, the passivating agent can be a conventional passivating agent in the art, preferably a mixture of a weakly acidic organic acid salt and an inorganic salt, wherein: the organic acid salt preferably comprises one or more of trisodium citrate, sodium salicylate and tetrasodium EDTA; preferably, the inorganic salt is preferably barium titanate; and more preferably, the passivating agent comprises trisodium citrate, sodium salicylate, tetrasodium EDTA and barium titanate.

[0024] Wherein, preferably, the aqueous solution comprising the passivating agent has a concentration of 10%-20%, wherein the concentration of the aqueous solution comprising the passivating agent is calculated by a mass percentage of the passivating agent in the aqueous solution comprising the passivating agent.

[0025] In S2, preferably, the passivation treatment is performed at a temperature of 25-50°C, more preferably 25-30°C.

[0026] In S2, preferably, the passivation treatment is performed for a time of 6-10 minutes, more preferably 8-10 minutes.

[0027] In S2, preferably, the passivation treatment is achieved by immersion or spraying; the immersion refers to immersing the permanent magnet in an aqueous solution comprising a passivating agent; the spraying refers to spraying the aqueous solution comprising a passivating agent on the permanent magnet.

[0028] In S2, preferably, the baking is performed at a temperature of 70-90°C, preferably 75-85°C.

[0029] In S2, preferably, the baking is performed for a time of 25-40min, preferably 25-35min.

[0030] In the present invention, the preparation process includes zirconization treatment and passivation treatment. After the zirconization treatment, a layer of locally dense zirconization film will be formed on the surface of the permanent magnet, but dried cracks will appear on its surface. A passivation film formed after the passivation treatment can cover its surface to form a closed layer, which will not damage the zirconization film, but can seal and fill the defects or weak points of the zirconization film, thereby repairing the cracks of the zirconization film. The above-mentioned inner and outer layers cooperate with each other to form a protective film with moisture resistance.

[0031] In the present invention, the aqueous solution comprising the zirconizing agent is acidic, while the aqueous solution comprising the passivating agent is alkaline. During the treatment process, mutual contamination between the two needs to be avoided.

[0032] In the present invention, the permanent magnet can be subjected to a pretreatment before the zirconization treatment, wherein preferably, the pretreatment includes the following steps in sequence: (1) grinding; (2) degreasing; (3) first water washing; (4) acid pickling and rust removal; (5) second water washing; and (6) ultrasonic dust removal.

[0033] In step (1), the grinding can be a conventional operation in the art.

[0034] In step (1), preferably, a rust inhibitor is added during the grinding process.

[0035] Wherein, the rust inhibitor may be a conventional rust inhibitor in the art; preferably, the rust inhibitor comprises one or more of sodium phosphate, sodium carbonate, sodium hydroxide and an OP-10 emulsifier; more preferably, the rust inhibitor comprises one or more of 60-80g/L of sodium phosphate, 40-60g/L of sodium carbonate, 5-10g/L of sodium hydroxide or 0.05-1g/L of the OP-10 emulsifier

[0036] In step (1), preferably, the grinding is performed in a vibrating grinder.

[0037] In step (1), preferably, the grinding is performed at a temperature of 10-40°C.

[0038] In step (1), preferably, the grinding is performed for a time of 2-36 h.

[0039] In step (2), the degreasing can be a conventional operation in the art.

[0040] In step (2), preferably, a degreasing powder is added during the degreasing process. Wherein, the degreasing powder can be a conventional degreasing powder in the art. In step (2), preferably, the degreasing is performed at a temperature of 45-55°C.

[0041] In step (2), preferably, the degreasing is performed for a time of 3-7 min.

[0042] In step (3), the first water washing can be a conventional operation in the art.

[0043] In step (3), preferably, the first water washing is performed in a first water washing tank and a second water washing tank respectively.

[0044] In step (3), preferably, the first water washing is performed for a time of 10-20 seconds.

[0045] In step (3), preferably, the first water washing has an overflow water flow of 100 cubic meters/hour.

[0046] In step (4), preferably, the acid pickling and rust removal is performed for a time of 30-50s.

[0047] In step (4), preferably, the acid pickling and rust removal is performed by using an acid being dilute nitric acid; more preferably, the dilute nitric acid has a concentration of 1%-3%.

[0048] In step (4), the acid pickling and rust removal is to remove the oxide layer on the surface of the permanent magnet, so as to facilitate the subsequent zirconization film to better adhere to the surface of the permanent magnet.

[0049] In step (5), the first water washing can be a conventional operation in the art.

[0050] In step (5), preferably, the second water washing is performed in a third water washing tank.

[0051] In step (5), preferably, the second water washing is performed for a time of 10-20 seconds.

[0052] In step (5), preferably, the second water washing has an overflow water flow of 100 cubic meters/hour.

[0053] In step (6), preferably, the ultrasonic dust removal is performed in a fourth water washing tank.

[0054] In step (6), preferably, before the ultrasonic dust removal, an ultrasonic protective agent is added. In the process of ultrasonic dust removal, adding an ultrasonic protective agent can achieve a better ultrasonic effect, so that the surface cleanliness of the magnet is higher, which is conducive to the subsequent film formation.

[0055] Wherein, the ultrasonic protective agent is a conventional ultrasonic protective agent in the art; preferably, the ultrasonic protective agent has a concentration of 0.1-1%, wherein the concentration of the ultrasonic protective agent is calculated by a mass percentage of the ultrasonic protective agent in the washing water in the fourth water washing tank.

[0056] In step (6), preferably, the ultrasonic dust removal is performed for a time of 2-5min. The present invention further provides a permanent magnet, which is obtained by the surface treatment method for a permanent magnet as described above.

[0057] The present invention further provides a permanent magnet protective film, which is obtained by the surface treatment method for a permanent magnet as described above.

[0058] On the basis of conforming to the common sense in the art, the above-mentioned preferred conditions can be arbitrarily combined to obtain the preferred embodiments of the present invention.

[0059] The reagents and raw materials used in the present invention are commercially available.

[0060] The positive and progressive effects of the present invention are as follows:

1. By adopting the process of the present invention, a protective film with extremely stable chemical properties can be formed on the surface of the neodymium-iron-boron material in a short time. The protective film has excellent corrosion resistance, and the film layer is densely crystallized, uniform, and has good rust resistance. In the air temperature and humidity alternating condensation test (ART test), the moisture-resistant time of the permanent magnet is more than 7 cycles (168h), and the appearance of the sample did not change color or have rust spots after the test.

2. By adopting the process of the present invention, the protective film on the surface of the permanent magnet obtained further has a larger surface tension, so that it has good adhesion in the subsequent application of the permanent magnet.

3. By adopting the process of the present invention, the concept of green ecological and environmentally friendly production is met, thereby avoiding the problem of sediment and the emission of a large amount of pollutants.

4. By adopting the process of the present invention, the obtained surface protective film having a double-layer structure of a zirconization layer and a passivation layer has better uniformity and appearance consistency.

BRIEF DESCRIPTION OF THE DRAWINGS

[0061]

Fig. 1 shows the pictures of the samples prepared in Example 1 before and after 15 cycles (360h) of testing in a wet heat box.

Fig. 2 shows the pictures of the samples prepared in Comparative Example 1 before and after 4 cycles (96h) of testing in a wet heat box.

Fig. 3 shows the pictures of the samples prepared in Comparative Example 2 before and after 5 cycles (120h) of

testing in a wet heat box.

DETAILED DESCRIPTION OF THE INVENTION

[0062] The present invention is further illustrated by way of examples below, but the present invention is not limited to the scope of the examples described. The experimental methods for which specific conditions are not specified in the following examples are selected according to the conventional methods and conditions or according to the product instructions.

Example 1

[0063] This example relates to a surface treatment method for a permanent magnet, which includes the following steps:

S0: Pre-treating the permanent magnet, including the following steps:

(1) The permanent magnet was put into a vibrating grinder for grinding and a rust inhibitor was added. The grinding temperature was 25°C and the grinding time was 10h. The rust inhibitor was 70g/L sodium phosphate, 50g/L sodium carbonate and 8g/L sodium hydroxide;

(2) The ground permanent magnet was mixed with a degreasing powder for degreasing. The degreasing temperature was 50°C and the degreasing time was 5min;

(3) The degreased permanent magnet was placed in a first washing tank and a second washing tank for the first washing in turn. The time of the first washing was 20s, and the overflow water flow of the first washing was 100 cubic meters/hour;

(4) The permanent magnet obtained after the first water washing was subjected to acid pickling and rust removal by using a 3% dilute nitric acid, wherein the time for the acid pickling and rust removal was 40s;

(5) The permanent magnet after the acid pickling and rust removal was placed in a third water washing tank for a second water washing, wherein the second washing time was 10s, and the overflow water flow of the second water washing was 100 cubic meters/hour;

(6) The permanent magnet after the second water washing was placed in a fourth water washing tank, and an ultrasonic protective agent was added for ultrasonic dust removal, wherein the time for the ultrasonic dust removal was 4 minutes, the concentration of the ultrasonic protective agent was 0.5%, and the concentration of the ultrasonic protective agent based on the mass percentage of the ultrasonic protective agent in the washing water in the fourth water washing tank;

S1: The pretreated permanent magnet prepared in S0 was placed in a zirconizing agent with a concentration of 50%, and zirconized for 15 minutes at 25°C and a pH value of 3.8, and a zirconized permanent magnet was obtained by immersion coating; the concentration of the zirconizing agent was based on the mass percentage of the zirconizing agent in the aqueous solution comprising the zirconizing agent; the zirconizing agent is a special zirconizing agent for rare earth neodymium-iron-boron materials, which comprised fluorozirconate and fluorozirconic acid and came from Hainan Hainan Hongxiang Industrial Co., Ltd.;

S2: Before the passivation treatment, the zirconized permanent magnet was subjected to a third water washing and drying; the time for the third water washing was 15 seconds; the overflow water flow of the third water washing was 100 cubic meters/hour; the drying temperature was 80°C; and the drying time was 30 minutes;

[0064] Subsequently, the passivation treatment was carried out by immersion in a passivation agent with a concentration of 20% for 8 minutes at 25°C and a pH value greater than or equal to 10, and then baked at a temperature of 80°C for 30 minutes; the zirconizing agent was a mixture of trisodium citrate, sodium salicylate, tetrasodium EDTA and barium titanate.

Example 2

[0065] The permanent magnet was pretreated by the step S0 in Example 1;

S1: The pretreated permanent magnet prepared in S0 was placed in a zirconizing agent with a concentration of 50%, and zirconized for 20 minutes at 5°C and a pH value of 3.5, and a zirconized permanent magnet was obtained by immersion coating; the concentration of the zirconizing agent was based on the mass percentage of the zirconizing agent in the aqueous solution comprising the zirconizing agent; the zirconizing agent is a special zirconizing agent for rare earth neodymium-iron-boron materials, which comprised fluorozirconate and fluorozirconic acid and came from Hainan Hainan Hongxiang Industrial Co., Ltd.;

S2: Before the passivation treatment, the zirconized permanent magnet was subjected to a third water washing and

drying; the time for the third water washing was 10 seconds; the overflow water flow of the third water washing was 100 cubic meters/hour; the drying temperature was 80°C; and the drying time was 30 minutes;

[0066] Subsequently, the passivation treatment was carried out by spraying using a passivation agent with a concentration of 20% for 4 minutes at 50°C and a pH value of 10, and then baked at a temperature of 80°C for 30 minutes; the zirconizing agent was a mixture of trisodium citrate, sodium salicylate, tetrasodium EDTA and barium titanate.

Example 3

[0067] The permanent magnet was pretreated by the step S0 in Example 1;

S1: The pretreated permanent magnet prepared in S0 was placed in a zirconizing agent with a concentration of 50%, and zirconized for 5 minutes at 40°C and a pH value of 3.5, and a zirconized permanent magnet was obtained by drum coating; the concentration of the zirconizing agent was based on the mass percentage of the zirconizing agent in the aqueous solution comprising the zirconizing agent; the zirconizing agent is a special zirconizing agent for rare earth neodymium-iron-boron materials, which comprised fluorozirconate and fluorozirconic acid and came from Hainan Hainan Hongxiang Industrial Co., Ltd.;

S2: Before the passivation treatment, the zirconized permanent magnet was subjected to a third water washing and drying; the time for the third water washing was 20 seconds; the overflow water flow of the third water washing was 100 cubic meters/hour; the drying temperature was 80°C; and the drying time was 30 minutes;

[0068] Subsequently, the passivation treatment was carried out by immersion or spraying using a passivation agent with a concentration of 20% for 12 minutes at 15°C and a pH value of 10, and then baked at a temperature of 80°C for 30 minutes; the zirconizing agent was a mixture of trisodium citrate, sodium salicylate, tetrasodium EDTA and barium titanate.

Comparative Example 1

[0069] Using the existing phosphating process, the surface of the permanent magnet was phosphated to obtain a permanent magnet.

Comparative Example 2

[0070] The treatment method of Example 1 was adopted. The difference between this comparative example and Example 1 was that the temperature of the zirconization treatment in step S1 was 50°C and the time of the zirconization treatment was 40 minutes.

Comparative Example 3

[0071] The treatment method of Example 1 was adopted. The difference between this comparative example and Example 1 was that the pH value of the zirconization treatment in step S1 was 7.

Comparative Example 4

[0072] The treatment method of Example 1 was adopted. The difference between this comparative example and Example 1 was that the temperature of the passivation treatment in step S2 was 10°C and the time of the passivation treatment was 10 minutes.

Comparative Example 5

[0073] The treatment method of Example 1 was adopted. The difference between this comparative example and Example 1 was that the pH value of the passivation treatment in step S2 was 9.

Effect Example 1

AHT Testing

[0074] The permanent magnets prepared in Examples 1-3 and Comparative Examples 1-5 were subjected to AHT testing, i.e., a condensation test for alternating changes in air temperature and humidity. The results are shown in Figures 1

to 3 and Table 1.

Fig. 1 shows the pictures of the samples prepared in Example 1 before and after 15 cycles (360h) of testing in a wet heat box. Fig. 1 (a) shows a picture showing the sample before the test, and Fig. 1 (b) shows a picture showing the sample after the test. The moisture-resistant time of the permanent magnet prepared in Example 1 reached more than 15 cycles (360 hours), and the appearance thereof did not show color change or rust spots after the test.

Fig. 2 shows the pictures of the samples prepared in Comparative Example 1 before and after 4 cycles (96h) of testing in a wet heat box. Fig. 2 (a) shows a picture showing the sample before the test, and Fig. 2 (b) shows a picture showing the sample after the test. After the permanent magnet of Comparative Example 1 had been in the wet heat box for 4 cycles (96h), although there were no rust spots on the surface thereof, obvious color change occurred, which is regarded as a sign to corrosion failure.

Fig. 3 shows the pictures of the samples prepared in Comparative Example 2 before and after 5 cycles (12h) of testing in a wet heat box. Fig. 3 (a) shows a picture showing the sample before the test, and Fig. 3 (b) shows a picture showing the sample after the test. After the permanent magnet of Comparative Example 2 was tested in the wet heat box for 5 cycles (120h), obvious red rust spots appeared on the surface.

Table 1

	AHT Testing Results
Example 1	The moisture-resistant time of the permanent magnet can reach 15 cycles (360h)
Example 2	The moisture-resistant time of the permanent magnet can reach 7 cycles (168h) or more
Example 3	The moisture-resistant time of the permanent magnet can reach 11 cycles (264h) or more
Comparative Example 1	After 4 cycles (96h) in the wet heat box, obvious color change appeared
Comparative Example 2	After 5 cycles (120h) in the wet heat box, red rust spots appeared
Comparative Example 3	After 2 cycles (48h) in the wet heat box, red rust spots appeared
Comparative Example 4	After 4 cycles (96h) in the wet heat box, red rust spots appeared
Comparative Example 5	After 4 cycles (96h) in the wet heat box, red rust spots appeared

Effect Example 2: Surface Tension Testing

[0075] The permanent magnets prepared in Examples 1-3 and Comparative Examples 1-5 were tested for surface tension by using the conventional dyne pen test method in the art to obtain the results shown in Table 2:

Table 2

	Surface Tension (mN/m)
Example 1	42
Example 2	40
Example 3	40
Comparative Example 1	40
Comparative Example 2	38
Comparative Example 3	38
Comparative Example 4	38
Comparative Example 5	38

[0076] It can be seen that the surface tension of the moisture-resistant protective films of the permanent magnets prepared by the processing method of the present application can reach 40 mN/m or above.

Claims

1. A surface treatment method for a permanent magnet, **characterized by** comprising the following steps of:

S1: subjecting the permanent magnet to zirconization treatment to obtain a permanent magnet having a zirconization film, wherein the zirconization treatment is performed at a temperature of 5-40°C for a time of 5-30 min at a pH value of 1.5-6; and

S2: subjecting the permanent magnet having the zirconization film to passivation treatment followed by baking, wherein the passivation treatment is performed at a temperature of 15-50°C for a time of 4-12 min at a pH value of greater than or equal to 10.

2. The surface treatment method for a permanent magnet according to claim 1, **characterized in that**, in S1:

the zirconization treatment is performed by immersing the permanent magnet in an aqueous solution comprising a zirconizing agent; and/or

the zirconization treatment is performed at a temperature of 20-30°C; and/or

the zirconization treatment is performed for a time of 10-25 min; and/or

the zirconization treatment is performed at a pH value of 3.2-5.5.

3. The surface treatment method for a permanent magnet according to claim 2, **characterized in that**, in S1:

the zirconizing agent comprises fluorozirconate and/or fluorozirconic acid; and/or the aqueous solution comprising the zirconizing agent has a concentration of 10%-60%, wherein the concentration of the aqueous solution comprising the zirconizing agent is calculated by a mass percentage of the zirconizing agent in the aqueous solution comprising the zirconizing agent; and/or

the immersing is direct immersing or indirect immersing; and/or the zirconization treatment is performed for a time of 15-20 min.

4. The surface treatment method for a permanent magnet according to claim 1, **characterized in that**, in S2:

before the passivation treatment, the permanent magnet having the zirconization film is successively subjected to a third water washing and drying; and/or

the passivation treatment is performed in an aqueous solution comprising a passivating agent; and/or

the passivation treatment is performed at a temperature of 25-50°C; and/or

the passivation treatment is performed for a time of 6-10 min; and/or

the passivation treatment is achieved by immersion or spraying; and/or

the baking is performed at a temperature of 70-90°C; and/or

the baking is performed for a time of 25-40 min.

5. The surface treatment method for a permanent magnet according to claim 4, **characterized in that**, in S2:

the third water washing is performed for a time of 10-20 seconds; and/or

the third water washing has an overflow water flow of 100 cubic meters/hour; and/or

the drying is performed at a temperature of 80°C; and/or

the drying is performed for a time of 30min; and/or

the passivating agent is a mixture of a weakly acidic organic acid salt and an inorganic salt, wherein: the organic acid salt preferably comprises one or more of trisodium citrate, sodium salicylate and tetrasodium EDTA; the inorganic salt is preferably barium titanate; and preferably, the passivating agent comprises trisodium citrate, sodium salicylate, tetrasodium EDTA and barium titanate; and/or

the aqueous solution comprising the passivating agent has a concentration of 10%-20%, wherein the concentration of the aqueous solution comprising the passivating agent is calculated by a mass percentage of the passivating agent in the aqueous solution comprising the passivating agent; and/or

the passivation treatment is performed at a temperature of 25-30°C; and/or

the passivation treatment is performed for a time of 8-10 min; and/or

the baking is performed at a temperature of 75-85°C; and/or

the baking is performed for a time of 25-35 min.

6. The surface treatment method for a permanent magnet according to claim 1, **characterized in that** the permanent

magnet is subjected to a pretreatment before the zirconization treatment, wherein the pretreatment includes the following steps in sequence: (1) grinding; (2) degreasing; (3) first water washing; (4) acid pickling and rust removal; (5) second water washing; and (6) ultrasonic dust removal.

7. The surface treatment method for a permanent magnet according to claim 6, **characterized in that**:

in step (1), a rust inhibitor is added during the grinding process; and/or
 in step (1), the grinding is performed in a vibrating grinder; and/or
 in step (1), the grinding is performed at a temperature of 10-40°C; and/or
 in step (1), the grinding is performed for a time of 2-36 h; and/or
 in step (2), a degreasing powder is added during the degreasing process; and/or
 in step (2), the degreasing is performed at a temperature of 45-55°C; and/or
 in step (2), the degreasing is performed for a time of 3-7 min; and/or
 in step (3), the first water washing is performed in a first water washing tank and a second water washing tank respectively; and/or
 in step (3), the first water washing is performed for a time of 10-20 seconds; and/or
 in step (3), the first water washing has an overflow water flow of 100 cubic meters/hour; and/or
 in step (4), the acid pickling and rust removal is performed for a time of 30-50s; and/or
 in step (4), the acid pickling and rust removal is performed by using an acid being dilute nitric acid; and/or
 in step (5), the second water washing is performed in a third water washing tank; and/or
 in step (5), the second water washing is performed for a time of 10-20 seconds; and/or
 in step (5), the second water washing has an overflow water flow of 100 cubic meters/hour; and/or
 in step (6), the ultrasonic dust removal is performed in a fourth water washing tank; and/or
 in step (6), before the ultrasonic dust removal, an ultrasonic protective agent is added; and/or
 in step (6), the ultrasonic dust removal is performed for a time of 2-5min.

8. The surface treatment method for a permanent magnet according to claim 7, **characterized in that**:

in step (1), the rust inhibitor comprises one or more of sodium phosphate, sodium carbonate, sodium hydroxide and an OP-10 emulsifier; preferably, the rust inhibitor comprises one or more of 60-80g/L of sodium phosphate, 40-60g/L of sodium carbonate, 5-10g/L of sodium hydroxide or 0.05-1g/L of the OP-10 emulsifier; and/or
 in step (4), the dilute nitric acid has a concentration of 1%-3%; and/or
 in step (6), the ultrasonic protective agent has a concentration of 0.1-1%, wherein the concentration of the ultrasonic protective agent is calculated by a mass percentage of the ultrasonic protective agent in the washing water in the fourth water washing tank.

9. A permanent magnet, **characterized in that** it is obtained by using the surface treatment method for a permanent magnet according to any one of claims 1 to 8.

10. A permanent magnet protective film, **characterized in that** it is obtained by using the surface treatment method for a permanent magnet according to any one of claims 1 to 8.

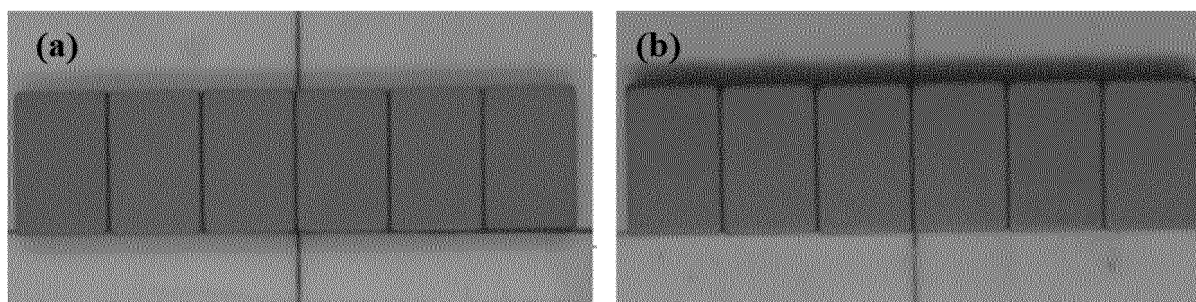


Fig. 1

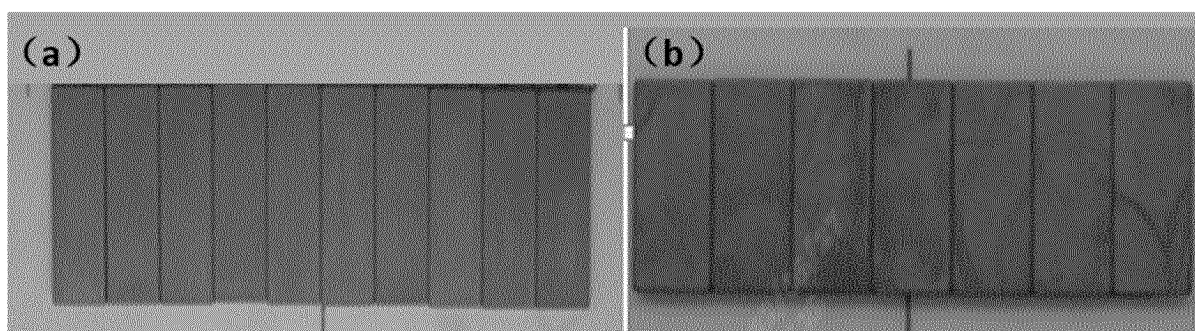


Fig. 2

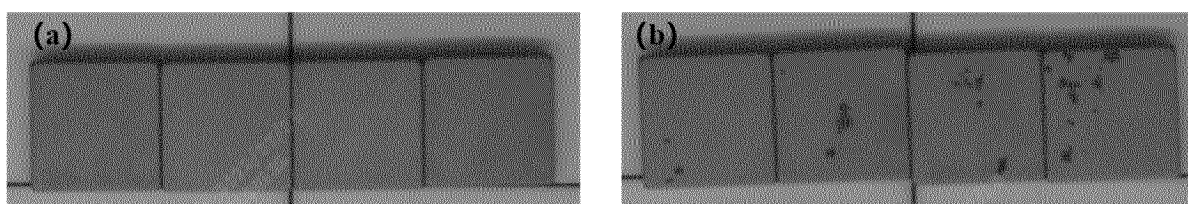


Fig. 3

INTERNATIONAL SEARCH REPORT

International application No.

PCT/CN2023/090163

A. CLASSIFICATION OF SUBJECT MATTER

C23C22/80(2006.01)i; C23C22/60(2006.01)i; H01F41/02(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC: C23C22/-, H01F41/-

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)

CNABS, CNKI, CNTXT, WPABS, DWPI, ENTXT: 永磁, 钕铁硼, 钕化, 氟钕酸, 钝化, 钛, 封闭, permanent, NdFeB, magnet, zirconium, Zr, fluozirconic, +ZrF6, passivat+, titanium, Ti, seal+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
PX	CN 115584496 A (FUJIAN CHANGJIANG GOLDEN DRAGON RARE EARTH CO., LTD.) 10 January 2023 (2023-01-10) claims 1-10	1-10
Y	CN 102453890 A (BEIJING ZHONG KE SAN HUAN HI-TECH CO., LTD. et al.) 16 May 2012 (2012-05-16) claim 1	1-10
Y	CN 10230049 A (ZHEJIANG NINE METAL SURFACE TREATMENT TECHNOLOGY CO., LTD.) 13 September 2019 (2019-09-13) description, paragraphs [0001]-[0033]	1-10
A	CN 102400125 A (INSTITUTE OF METAL RESEARCH, CHINESE ACADEMY OF SCIENCES) 04 April 2012 (2012-04-04) entire document	1-10
A	CN 109989053 A (BEIJING ZHONG KE SAN HUAN HI-TECH CO., LTD.) 09 July 2019 (2019-07-09) entire document	1-10

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

* Special categories of cited documents:

“A” document defining the general state of the art which is not considered to be of particular relevance

“D” document cited by the applicant in the international application

“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

Date of the actual completion of the international search

19 May 2023

Date of mailing of the international search report

01 June 2023

Name and mailing address of the ISA/CN

China National Intellectual Property Administration (ISA/
CN)China No. 6, Xitucheng Road, Jimenqiao, Haidian District,
Beijing 100088

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2023/090163

5

10

15

20

25

30

35

40

45

50

55

C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 114774903 A (ZHEJIANG UNIVERSITY OF TECHNOLOGY) 22 July 2022 (2022-07-22) entire document	1-10
A	US 2005233068 A1 (YOSHIMURA KOHSHI et al.) 20 October 2005 (2005-10-20) entire document	1-10

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.

PCT/CN2023/090163

5

10

15

20

25

30

35

40

45

50

55

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 115584496 A	10 January 2023	None	
CN 102453890 A	16 May 2012	None	
CN 110230049 A	13 September 2019	None	
CN 102400125 A	04 April 2012	None	
CN 109989053 A	09 July 2019	None	
CN 114774903 A	22 July 2022	None	
US 2005233068 A1	20 October 2005	US 2008124567 A1	29 May 2008
		US 7335392 B2	26 February 2008
		KR 20050083572 A	26 August 2005
		KR 101073326 B1	12 October 2011
		AU 2003302524 A1	23 June 2004
		EP 1511046 A1	02 March 2005
		EP 1511046 A4	22 April 2009
		EP 1511046 B1	20 May 2015
		WO 2004051678 A1	17 June 2004