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(54) Title: AGING-RESISTANT PERMANENT MAGNET MADE FROM AN ALLOY POWDER AND METHOD FOR PRODUCING SAME

(54) Bezeichnung: ALTERUNGSBESTÄNDIGER DAUERMAGNET AUS EINEM LEGIERUNGSPULVER UND VERFAHREN ZU SEINER HERSTELLUNG

(57) Abstract: The invention relates to a method for producing pressed permanent magnets, comprising the following steps: providing a mixture of at least one magnetic powder and one duroplastic binder and pressing said mixture to form a moulding body. In order to obtain a durable and particularly reliable protection against oxidation and corrosion, the moulding body is impregnated with an acid-solvent mixture in an impregnation bath before hardening of the duroplastic binder, whereby the entire surface of the permanent magnet is covered with a reaction layer.

(57) Zusammenfassung: Ein Verfahren zur Herstellung von gepressten Dauermagneten umfasst folgende Schritte: Es wird ein Gemisch zumindest aus einem Magnetpulver und einem duroplastischen Binder bereitgestellt und zu einem Formkörper gepresst. Um einen dauerhaften und besonders zuverlässigen Oxidations- und Korrosionsschutz zu erreichen, wird der Formkörper vor dem Aushärten des duroplastischen Binders in einem Imprägnierbad mit einem Säure-Lösungsmittel-Gemisch imprägniert und auf diese Weise die gesamte Oberfläche des Dauermagneten mit einer Reaktionsschicht überzogen.

WO 2007/122590 A1

Description

Non-ageing permanent magnet made from an alloy powder and method for the production thereof

The invention relates to a permanent magnet pressed from an alloy powder and a thermosetting binder. It further relates to a method for the production of such a permanent magnet.

Permanent magnets which consist of an alloy powder, in particular a rare earth powder, and possibly of further additives, and which are bonded using a plastic material, can be produced in a great variety of precisely predetermined shapes by means of injection moulding or pressing technology without requiring any complex and costly reworking. Pressed permanent magnets, in particular permanent magnets pressed in a mould at ambient temperature and without heated tools from the alloy powder and a thermosetting binder and then cured, have particularly good magnetic properties and can moreover be produced very economically using very short cycle times.

Such pressed permanent magnets are, however, porous, which may result in oxidation or corrosion, for example by air and humidity, both in the curing process and in later use, in particular at elevated temperatures. The result is an ageing of the permanent magnet accompanied by a worsening of its magnetic properties. The term "ageing" of the magnet is here understood to mean a reduction of its magnetic properties in the course of time, in particular at elevated operating temperatures.

The ageing of the magnet can be inhibited by avoiding high operating temperatures. This limiting of the operating temperatures to, for example, 100°C is, however, undesirable, as it prevents the application of pressed permanent magnets in many desirable fields, such as motors.

Various approaches have so far only resulted in insufficient and temporary protection of the permanent magnet against oxidation and corrosion. A thin coating for the finished magnet has been shown to be permeable and moreover easily damaged.

EP 1 583 111 A1 discloses a method for the production of pressed permanent magnets, wherein the individual powder particles are provided with a protective coating prior to the pressing process. However, as the coating is damaged in many places in the pressing process, resulting in new uncoated surfaces, a sufficient protection against oxidation and corrosion cannot be ensured. Even an additional impregnation with a synthetic resin as known from JP 63304602-A cannot ensure reliable and permanent protection.

The invention is therefore based on the problem of specifying a method whereby permanently oxidation- and corrosion-resistant permanent magnets can be produced in a simple manner.

The present invention is further based on the problem of specifying a pressed permanent magnet with a particularly effective oxidation and corrosion protection, which can be used in temperatures above 100°C without ageing prematurely.

According to the invention, these problems are solved by the subject matter of the independent patent claims. Advantageous further developments of the invention are the subject matter of the dependent claims.

A method according to the invention for the production of magnets comprises the following steps: First, a mixture of a magnetic powder and a thermosetting binder is provided and pressed to produce a moulded body of a desired shape. This moulded body is then exposed to a mixture of acid and solvent in an impregnating bath. The thermosetting binder is then cured. Suitable acids include phosphoric acid, oxalic acid, boric acid and chromic acid.

According to an idea on which the invention is based, the entire surface of the magnet, which forms an interface with an ambient atmosphere and thus a surface affected by oxidising and corrosive substances, should be protected to provide an effective protection against oxidation and corrosion, i.e. in particular the internal surfaces of the magnet or the particles of which it consists. In place of a protective

coating, which, in view of the resulting deviation from the original shape of the magnet, has to be very thin and is therefore easily damaged, the interface should be protected by a protective layer formed by the action of an acid, such as a phosphating layer. In place of or in addition to phosphate, the protective layer may comprise molybdate, tungstate, titanate, oxalate, chromate or combinations thereof. Such a protective layer can be applied to the entire interface by immersing the porous moulded body in an impregnating bath containing a mixture of acid and solvent. Owing to its low viscosity, this mixture of acid and solvent reaches the surface including the entire accessible interstitial space and thus the whole magnet surface which may be affected by oxidising and corrosive substances.

The method according to the invention therefore protects the entire vulnerable surface by coating – if possible immediately after the pressing process – the metal surfaces accessible to corrosive substances such as oxygen and humidity by means of a chemical reaction under the participation of phosphoric acid. The penetration of substances into the accessible interstitial space is used to advantage in the impregnation process.

The moulded body is advantageously retained in the impregnating bath for at least 15 minutes, for example for 30 minutes. This ensures the formation of a sufficiently thick phosphating layer for the passivation of the surface. The retention time can be reduced by tempering the impregnating bath.

The impregnating solution, which advantageously has a composition of 2 to 6 percent by weight of 85%-phosphoric acid, preferably orthophosphoric acid H_3PO_4 , 1 to 2 percent by weight of distilled water, rest alcohol or another common solvent, or even just phosphoric acid dissolved or dispersed in water, enters the externally accessible interstitial space of the pressed body as a result of the capillary effect. This effect can, however, be additionally supported by exposing the impregnating bath with the moulded body to a vacuum during the impregnation process. This vacuum promotes the escape of air from the interstitial space and accelerates the flow of impregnating agents into the pores. This flow can be improved further by introducing a gas into the space above the impregnating bath following the removal of air from the interstitial space, whereby a positive pressure is generated.

In one embodiment of the invention, the magnetic powder used is a metal or alloy powder, in particular a hard magnetic alloy powder. The magnetic powders used in a preferred embodiment are Nd-Fe-B alloy powders, which contain the hard magnetic phase $\text{Nd}_2\text{Fe}_{14}\text{B}$ and are for example produced in accordance with the rapid solidification process or the hydrogenation disproportionation desorption recombination (HDDR) process. In this process, which is described in detail in US 6,709,533 B2, the relatively coarse structure of the molten material initially disintegrates in a hydrogen atmosphere and then recombines to form a very fine-grained structure, while the crystal orientation of the original grain is maintained.

Alloys of samarium and cobalt containing the hard magnetic phases $\text{Sm}_2\text{Co}_{17}$ and/or Sm_1Co_5 can be used as alternatives.

The average particle size d of the magnetic powder advantageously is $50\text{ }\mu\text{m} \leq d \leq 150\text{ }\mu\text{m}$. This average particle size allows for an advantageous packing density of 75% to 80% volume ratio. Finer and coarser powders tend to have worse magnetic properties and age more quickly. For additional protection against ageing, the particles of the magnetic powder may be coated even before the impregnation process, for example with a phosphating layer.

The mixture is advantageously pressed to produce a moulded body under a pressure of 8 t/cm^2 at room temperature. In this process, the mixture can be exposed to a magnetic field.

The moulded body is for example cured at a temperature of at least 170°C , typically in an oven in the presence of air. The curing process takes approximately 60 minutes. The curing conditions are determined by the type of thermosetting material.

In a further embodiment, the impregnation process using the mixture of phosphoric acid and solvent is followed by a second impregnation step, wherein the moulded body is additionally impregnated with an epoxy resin. Between its impregnation with the mixture of phosphoric acid and solvent and the second impregnation step and/or

before the curing of the thermosetting binder, the moulded body is advantageously dried, for example by evacuation. The acidic impregnating solution may, however, already contain a dissolved or dispersed plastic substance, for example a thermosetting resin. The resistance to ageing of the magnet according to the invention can be improved further if inorganic components such as silanes or titanates are added to the impregnating solution either concurrently or in a further step.

The method according to the invention offers the advantage that the surface can be coated with a protective layer in a particularly simple and effective way and without any major technical effort by using an impregnating bath. The coating process can further be accelerated and/or enhanced in a simply way by the use of pressure differentials. The method permits the complete coating of the permanent magnet including the externally accessible interstitial space with a reaction layer, whereby the magnets produced in this way are reliably protected against oxidation and corrosion.

According to the present invention, a pressed, porous permanent magnet made from a rare earth alloy powder and a thermosetting binder has a surface representing an interface with an ambient atmosphere, wherein this surface of the permanent magnet is coated with a reaction layer, preferably a phosphating layer.

As rare earth alloy powders, Nd-Fe-B alloys, which contain the hard magnetic phase $\text{Nd}_2\text{Fe}_{14}\text{B}$ and are for example produced in accordance with the rapid solidification process or the hydrogenation disproportionation desorption recombination (HDDR) process, or alloys of samarium and cobalt, which contain the hard magnetic phases $\text{Sm}_2\text{Co}_{17}$ and/or Sm_1Co_5 , can be provided.

The permanent magnet according to the invention may have a remanence of 1.0 T and a coercitive field strength of 1060 kA/m. Its high energy product combined with a high dimensional stability resulting from the pressing process opens up a great variety of applications, for example in motors. The durably high load carrying capacity even at elevated temperatures, which is required for such applications, is ensured by the phosphating layer.

Embodiments of the invention are explained in greater detail below with reference to the accompanying figures.

Figure 1 is a flow chart of preferred embodiments of the method for the production of permanent magnets;

Figure 2 is a diagrammatic representation of the chronological development of the apparent remanence J_r' of Nd-Fe-B permanent magnets according to the invention;

Figure 3 is another diagrammatic representation of the chronological development of the apparent remanence J_r' of Nd-Fe-B permanent magnets according to the invention;

Figure 4 is a diagrammatic representation of the chronological development of the change of the magnetic flux of Nd-Fe-B permanent magnets according to the invention; and

Figure 5 is a diagrammatic representation of the chronological development of the ageing losses of Sm-Co permanent magnets according to the invention.

In a first embodiment of the method, which is identified as “example 1” in Figure 1, a mixture of 1.6 percent by weight of a thermosetting binder with the rest being a rare earth magnetic powder such as HDDR-Nd-Fe-B powder and various additives, if applicable, is oriented in a magnetic field and then pressed under a pressure of 8 t/cm^2 at room temperature to produce a moulded body with the dimensions $10 \times 10 \times 8.5 \text{ mm}$. The moulded body has a magnetic packing density of 75% and a porosity of approximately 17%.

After the pressing process, the moulded body is placed in a solution consisting of 4 percent by weight of 85% phosphoric acid, 1.2 percent by weight of distilled water and 94.8 percent by weight of isopropanol. The isopropanol may be replaced by another solvent, such as acetone, ethanol, butanol or water. This step is identified in Figure 1 as “S-impregnation”, an abbreviation for acid (Säure-) impregnation. During the impregnating process, the container with the impregnating solution and the

moulded body is subjected to a vacuum of 150 mbar to facilitate the escape of air from and the entry of the impregnating solution into the interstitial space. After 30 minutes, the moulded body is removed, dried by evacuation and then cured in an oven for 60 minutes at a temperature of 170°C in the presence of air.

In a second embodiment of the method, which is identified as “example 2” in Figure 1, an additional impregnating step is added between the drying process and the curing process. In this second impregnating step, the moulded body is impregnated in a bath with a liquid, low-viscosity two-component epoxy resin. This step is identified in Figure 1 as “K-impregnation”, an abbreviation for plastic (Kunststoff-) impregnation. Initially, a vacuum of approximately 800 mbar supports the escape of air from the interstitial space, and then a positive pressure of approximately 200 mbar accelerates the entry of the resin into the pores. The cure is identical to example 1, but at a temperature of 190°C.

In a third embodiment, which is identified as “example 3” in Figure 1, the method is carried out as in example 2, but the drying step between the two impregnating steps is omitted.

In a fourth embodiment, which is identified as “example 4” in Figure 1, the moulded body is at least partially subjected to a first curing step before impregnation. This offers the advantage that the moulded body is less vulnerable when being handled in the impregnating and drying steps. Minor oxidation and corrosion damage may, however, have to be tolerated, because the moulded body is subjected to high temperatures and possibly to air before being protected by impregnation. After the impregnating and drying processes, the curing of the moulded body is completed.

Figure 1 describes possible variants of the method by way of example only.

Combinations thereof and further process steps are conceivable, for example if additional coatings are to be applied to the moulded body or certain properties of the moulded body are to be adjusted to requirements. Working in a protective atmosphere is also conceivable, for example if the curing step has to be carried out before impregnation.

Figures 2 to 5 show the results of series of measurements aimed at improving the resistance to ageing of the permanent magnets according to the invention, Figures 2 to 4 representing measurements on permanent magnets made from an Nd-Fe-B powder and Figure 5 representing measurements on permanent magnets made from an Sm-Co magnetic powder.

Figure 2 illustrates the chronological development of the apparent remanence J_r' of a permanent magnet according to the invention, which is a measure for ageing. The values illustrated by broken lines represent the ageing of permanent magnets produced using the methods according to examples 1, 2 and 3 in Figure 1, while the values illustrated by a continuous line represent the ageing of a permanent magnet produced conventionally, i.e. not impregnated using the method according to the invention. The graphs relating to the values obtained from the method according to the invention are very close to one another and almost merge. This figure therefore shows clearly that the improvement obtainable by using the method according to the invention over conventional methods is greater than the spread of the values measured on permanent magnets produced using different variants of the method according to the invention.

Three permanent magnets were produced in accordance with each of the three methods according to the invention and with a conventional method. In each case, the average of the measured values of the three permanent magnets was plotted. All magnets were stored at approximately 120°C in the presence of air to represent a realistic loading of the magnets, and the apparent remanence J_r' was measured at varying time intervals. The series of measurements shown in Figure 3 follow the same pattern, but all magnets were magnetised before each measurement.

Figures 2 and 3 show that the losses in the apparent remanence J_r' , which are a measure for the ageing of the magnets, are noticeably lower for the magnets according to the invention than for the non-impregnated magnets. The open triangles mark values measured on magnets impregnated with a plastic material in addition to their

acid impregnation. The ageing losses of these magnets are slightly higher than those of cores exclusively impregnated with acid.

Figure 4 shows the chronological development of the losses in magnetic flux as a measurement for ageing losses based on permanent structural damage; the magnets were magnetised before each measurement. The graph shows that the magnets produced using the method according to the invention, the values of which are indicated by broken lines, show losses of less than 1% after more than 1000 hours, while the conventionally produced magnets show average losses of approximately 4.7%.

Figure 5 illustrates ageing losses of the apparent remanence J_r' on the example of a magnet produced using the method according to the invention from a powder with the alloy composition $\text{Sm}_2\text{Co}_{17}$ consisting of 15% Fe, 25.2% Sm, rest Co, the powder having an average particle size of 110 μm . The magnet was produced in accordance with the variant of example 1 in Figure 1. Magnets were produced from the same powder but without impregnation as comparative examples for the series of measurements shown in Figure 5. As in the other figures, the results of the measurements on the magnets according to the invention are indicated by broken lines, while the results of the reference measurements are indicated by a continuous line. Figure 5 shows that resistance to ageing can be improved significantly by impregnation in the Sm-Co magnets as well.

Claims

- [1] Method for the production of magnets, comprising the following steps:
- the provision of a mixture of at least one magnetic powder and a thermosetting binder;
 - pressing to produce a porous moulded body;
 - the impregnation of the moulded body in an impregnating bath with a solution containing an acid;
 - the curing of the thermosetting binder.
- [2] Method according to claim 1,
characterised in that
the solution containing an acid contains phosphoric acid.
- [3] Method according to claim 1 or 2,
characterised in that
the impregnating bath has a composition of 2 to 6 percent by weight of 85%-phosphoric acid, 1 to 2 percent by weight of distilled water and rest alcohol.
- [4] Method according to any of claims 1 to 3,
characterised in that
the retention time of the moulded body in the impregnating bath is at least 15 minutes.
- [5] Method according to any of claims 1 to 4,
characterised in that
the impregnating bath with the moulded body is subjected to a vacuum and/or to a positive pressure during the impregnation process.
- [6] Method according to any of claims 1 to 5,
characterised in that
a metal or alloy powder is used as a magnetic powder.

- [7] Method according to any of claims 1 to 6,
characterised in that
a hard magnetic alloy powder is used as a magnetic powder.
- [8] Method according to any of claims 1 to 7,
characterised in that
an alloy powder of neodymium, iron and boron containing the hard magnetic
phase $\text{Nd}_2\text{Fe}_{14}\text{B}$ is used as a magnetic powder.
- [9] Method according to any of claims 1 to 8,
characterised in that
an alloy powder of samarium and cobalt containing the hard magnetic phase
 $\text{Sm}_2\text{Co}_{17}$ or Sm_1Co_5 is used as a magnetic powder.
- [10] Method according to any of claims 1 to 9,
characterised in that
the average particle size d of the magnetic powder is $50\text{ }\mu\text{m} \leq d \leq 150\text{ }\mu\text{m}$.
- [11] Method according to any of claims 1 to 10,
characterised in that
a coating is applied to the particles of the magnetic powder.
- [12] Method according to any of claims 1 to 11,
characterised in that
the impregnating bath with the moulded body is subjected to a positive
pressure after the application of the vacuum.
- [13] Method according to any of claims 1 to 12,
characterised in that
the mixture is pressed at room temperature to produce a moulded body at a
pressure of 6 t/cm^2 or more.
- [14] Method according to any of claims 1 to 13,

characterised in that
the mixture is exposed to a magnetic field during the pressing process.

- [15] Method according to any of claims 1 to 14,
characterised in that
the moulded body is cured in the presence of air at a temperature of at least 120°C.
- [16] Method according to any of claims 1 to 15,
characterised in that
a second impregnation step with an epoxy resin follows the impregnation of the moulded body with the phosphoric acid and solvent mixture.
- [17] Method according to claim 16,
characterised in that
the moulded body is dried between its impregnation with the phosphoric acid and solvent mixture and the second impregnation step.
- [18] Method according to any of claims 1 to 17,
characterised in that
the solution containing an acid contains a plastic material and/or organic components.
- [19] Method according to any of claims 1 to 17,
characterised in that
the solution containing an acid contains inorganic components.
- [20] Pressed, porous permanent magnet made from a rare earth alloy powder and a thermosetting binder,
characterised in that
the surface of the permanent magnet which forms an interface with the ambient atmosphere is coated with a protective layer formed by a reaction with an acid.

- [21] Permanent magnet according to claim 20,
characterised in that
the protective layer contains phosphate.
- [22] Permanent magnet according to claim 20,
characterised in that
the protective layer contains molybdate.
- [23] Permanent magnet according to claim 20,
characterised in that
the protective layer contains tungstate.
- [24] Permanent magnet according to claim 20,
characterised in that
the protective layer contains vanadate.
- [25] Permanent magnet according to claim 20,
characterised in that
the protective layer contains titanate.
- [26] Permanent magnet according to any of claims 20 to 25,
characterised in that
a powder of neodymium, iron and boron with the composition $\text{Nd}_2\text{Fe}_{14}\text{B}$
produced in accordance with a hydrogenation disproportionation desorption
recombination (HDDR) process is provided as a rare earth alloy powder.
- [27] Permanent magnet according to any of claims 20 to 25,
characterised in that
a powder of samarium and cobalt with the composition $\text{Sm}_2\text{Co}_{17}$ or Sm_1Co_5
is provided as a rare earth alloy powder.