



(11)

EP 4 066 963 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
05.10.2022 Bulletin 2022/40

(21) Application number: **21165521.2**

(22) Date of filing: **29.03.2021**

(51) International Patent Classification (IPC):

B22F 1/00 ^(2022.01)	B22F 1/02 ^(2006.01)
B22F 8/00 ^(2006.01)	B22F 9/02 ^(2006.01)
C22C 38/00 ^(2006.01)	C23C 16/00 ^(2006.01)
C30B 29/52 ^(2006.01)	H01F 1/057 ^(2006.01)
H01F 41/02 ^(2006.01)	C22B 7/00 ^(2006.01)
C22B 59/00 ^(2006.01)	B22F 9/00 ^(2006.01)

(52) Cooperative Patent Classification (CPC):

(C-Sets available)

**B22F 8/00; B22F 1/05; B22F 1/145; B22F 1/16;
B22F 1/17; B22F 9/023; C22C 38/00; C23C 16/00;
H01F 1/0572; H01F 1/0573; H01F 41/0253;
H01F 41/0293; B22F 2009/001; B22F 2998/10;
B22F 2999/00;** (Cont.)

(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 MK MT NL NO
PL PT RO RS SE SI SK SM TR**
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(71) Applicant: **Jozef Stefan Institute
1000 Ljubljana (SI)**

(72) Inventors:

- **Zuzek Rozman, Kristina
1000 Ljubljana (SI)**
- **Sturm, Saso
1000 Ljubljana (SI)**

(74) Representative: **Gagel, Roland
Patentanwalt Dr. Roland Gagel
Landsberger Strasse 480a
81241 München (DE)**

(54) **METHOD OF FORMING A STARTING MATERIAL FOR PRODUCING RARE EARTH PERMANENT MAGNETS FROM RECYCLED MATERIALS AND CORRESPONDING STARTING MATERIAL**

(57) The present invention relates to a method of forming a starting material for producing rare earth permanent magnets from recycled materials. The method comprises at least the steps of providing single Nd₂Fe₁₄B grains of end-of-life Nd₂Fe₁₄B magnets and/or magnet scraps and coating the grains with a single layer or with a layer sequence of one or several grain boundary ma-

terials such that said single layer or layer sequence is covering each individual grain. The grain boundary material of said single layer or of a lowermost layer of said layer sequence is selected from one or several metals or metal compounds or alloys. The coated grains are then condensed to bulk Nd-Fe-B permanent magnets, optionally via subsequent thermal treatments.

EP 4 066 963 A1

(52) Cooperative Patent Classification (CPC): (Cont.)
C22C 2200/00; C22C 2202/02

C-Sets

B22F 2998/10, B22F 1/145, B22F 9/023,
B22F 8/00;
B22F 2999/00, B22F 1/145, B22F 1/17;
B22F 2999/00, B22F 1/145, B22F 1/17,
B22F 1/102, B22F 1/16;
B22F 2999/00, B22F 1/145, C22C 2202/02,
C22C 2200/00, B22F 1/05;
B22F 2999/00, C22C 2202/02, B22F 8/00;
B22F 2999/00, C22C 2202/02, B22F 2009/001

Description

Field of the Invention

[0001] The present invention relates to a method for reprocessing of recycled $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains from bulk sintered Nd-Fe-B magnets and/or magnet scraps, to form a starting material for novel high-performance permanent magnets with better corrosion resistance via conventional and novel sintering routes. The invention also relates to the structure of the starting material.

[0002] Securing sustainable access to Critical Raw Materials (CRMs) is one of the most serious challenge facing the materials sector right now. The vast majority of the rare earth elements (REEs) used in many regions are imported to produce permanent magnets (PMs) as vital components for a large range of electrical devices, and are central to "green revolution" innovations including turbines for energy conversion, and motors for electric mobility. The demand for REEs for making new PMs is projected to double in period 2020-2035, with a great increase in the availability of magnetic scrap as many new devices start entering their end-of-life (EOL). Yet, the overall recycling rates of magnets are close to zero, leading to a fatal import dependency of materials for PMs. The need for methods to recycle and reclaim CRMs from magnets is becoming urgent as the first generation of electric vehicles will begin to reach EOL in only five years. Combined with the need for new material sources, the drive towards improving efficiency, lightweight, and smaller-sized devices has shifted the focus on magnetic material technologies with energy densities peaking at $\sim 450 \text{ kJ/m}^3$ for neodymium-iron-boron (Nd-Fe-B) magnets in the early 2000s. Further approaches to maximize energy densities at various operating temperatures, e.g. other alloys, textured nanocomposites or grain boundary diffusion processes, so far delivered only incremental improvements at significantly higher manufacturing costs.

[0003] The present invention addresses both challenges simultaneously, reducing dependency on newly mined REE CRMs, while delivering novel starting material for novel permanent magnets with improved corrosion behaviour and an increased energy product at the same time, thus surpassing substantially the existing belief that Nd-Fe-B type material has come to its technical limits with respect to energy density.

Background of the Invention and Prior Art

[0004] The improvement of the PMs performance measured as the energy density product BH_{max} (a figure of merit for permanent magnets); has improved significantly during time and today's strongest PMs like Nd-Fe-B ($\text{Nd}_{14}\text{Fe}_{80}\text{B}_6$) reach as high as 450 kJ/m^3 . These magnets possess a great versatility when it comes to applications that arises from the fine-tuning of their chemical composition by adding some Dy, Tb, Gd, Nb, Co, Cu, Ga, and Al that modify some of the physical and magnetic

properties [1]. As stated in [2] the addition of Gd is known to improve the temperature coefficient of the coercivity. Cu and Al are added to Nd-Fe-B to improve sintering of the magnet alloy, while Nb is added for refining of the magnetic grains. Ga is added as it improves the intrinsic coercivity and the hot workability of the alloy and Co is added to increase the Curie temperature of Nd-Fe-B PMs.

[0005] The mechanism for the coercivity has been thought to develop due to the magnetic isolation of individual $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains ($\sim 90\%$ of the magnet) with a Nd-rich grain boundary (GB) surrounding the grains ($\sim 10\%$ of the magnet). Typically such a Nd-Fe-B PM would contain about 31-32 wt. % of the total rare-earth elements (REEs) concentration in the PM mainly Nd + Pr plus a few minor, heavy rare-earth elements (HREEs) such as Dy, Tb, and Gd [2], that exceeds the stoichiometric composition $\text{Nd}_2\text{Fe}_{14}\text{B}$ that contains 26,7 wt. % Nd, 73,2 wt. % Fe and 0.1 wt. % B by $\sim 5\text{-}6$ wt. %. Further with fully dense sintered magnets, the non-magnetic Nd-rich phase plays a major role in the production of REE PMs with good magnetic properties: in a liquid-phase sintering process that is taken into an advantage in conventional Nd-Fe-B PMs processing, it wets the surface of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ matrix grains, aiding to enhanced diffusion of atoms to promote densification, smoothing grain boundaries to limit the deleterious effects of local demagnetising fields at sharp edges, and providing a thin, smooth, defect-free grain boundary layer in order to magnetically insulate the $\text{RE}_2\text{Fe}_{14}\text{B}$ crystallites and provide a barrier to demagnetisation of neighbouring grains [3]. As a result, the choice of materials for grain boundary improvement is limited to those that form a liquid phase with comparable properties to (NdDy) during conventional sintering and ensures significant GB wetting as stated in [4] and the references within. Nd-rich phase is however prone to oxidation during the magnet's lifespan, resulting in Nd-Fe-B magnet scraps to have a higher oxygen content ($\sim 2000\text{-}5000 \text{ ppm}$) compared to the virgin magnets ($\sim 300\text{-}400 \text{ ppm}$), that leads to poor mechanical and magnetic properties. As it is predicted the nucleation of the reverse magnetization i.e. the magnetic domains occurs at a locally low-anisotropy regions with defects or at an area adjacent to non-ferromagnetic grains with a higher stray field, the coercivity (H_c) of sintered magnets $\sim 1.2 \text{ T}$ ($1\text{T} = 7961 \text{ kA/m}$) is only $\sim 20\%$ of the anisotropy field of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase ($\mu_0 H_A \sim 7 \text{ T}$) called the Brown paradox of magnetism [5]. To aim at high operational temperatures of the traction motors for (hybrid) and full electric vehicles which is approximately 200°C , the Nd-Fe-B ternary-based sintered magnet cannot be used due to the thermal degradation of coercivity. To achieve still an enough high coercivity at elevated temperatures one would require at least $H_c = 3 \text{ T}$ i.e. $\sim 2400 \text{ kA/m}$ at room temperature. Such demanded increment in the coercivity is however theoretically possible by substituting approximately one-third of the Nd atoms with the heavy rare earths (HREE) Dy or Tb in order to exploit the higher-

anisotropy field of the $(\text{Nd,Dy/Tb})_2\text{Fe}_{14}\text{B}$ phase [1]. But, when substituting Nd with Dy or Tb, the remanent magnetization decreases because of the antiferromagnetic coupling of the Dy and Tb with the Fe [6], causing the maximum room temperature energy product to fall to 250 kJ/m³ [5]. In order to increase the coercivity without sacrificing too much magnetisation, it is necessary to locally add the Dy and Tb, originations from Dy₂O₃, Tb₃O₄, DyF₃, or TbF₄ using the grain-boundary diffusion process (GBDP) [7-14]. Dy, Tb are added in small amounts (few % wt.) on the surface of the already sintered Nd-Fe-B magnets, where they are diffused along the grain boundaries towards magnet interior substituting a part of Nd in the Nd₂Fe₁₄B phase forming the so-called core shell structure of the Dy, Nd₂Fe₁₄B surrounding the Nd₂Fe₁₄B phase. Through the optimization of the DyF₃-layer thickness and a post-deposition heat treatment that leads to grain-boundary diffusion, the coercivity was increased by 30% with the addition of only 0.2 wt. % Dy [15, 16]. Since Nd-Fe-B PMs discovery in the 80' the studies on the coercivity mechanism in Nd-Fe-B PMs considered the demagnetization mechanism to be nucleation of the reversed magnetization domains [17]. However, in 2012 the group from NIMS in Tsukuba, proposed a mechanism of the magnetization reversal via domain wall pinning. They implied that the grain boundary phase separating the matrix grains is in fact ferromagnetic instead of paramagnetic that supported the reversed magnetization nucleation mechanism [18]. Taking this idea ahead, the interfaces between the Nd₂Fe₁₄B phase and the Nd-rich phase could play a crucial role in the magnetization reversal and thus determining the coercivity [5]. However, as the conventional powder metallurgy approaches [19] use the Nd-Fe-B phase diagram, that assures the Nd-rich GB phase to be in sufficient amounts. So the tailoring of the Nd-Fe-B microstructure outside of the phase equilibria was up to date impossible. There were however reports on modifying the Nd-rich GB phase, but they were limited to thin films [20], because pure Nd₂Fe₁₄B phase was not available. On top, thin films are in fact not the most appropriate system to study bulk magnetism effects as they are burdened with the shape-prevailing-effects. If, however the single-crystal Nd₂Fe₁₄B matrix grains can be recovered for example by recycling of EOL sintered Nd-Fe-B magnets, grain smoothing processes have already happened during the primary production, giving a new degree of freedom to use other materials as grain boundary phase to insulate the grains according to the present invention, and to tailor the magnetic properties during remanufacturing. Such grain recovery is possible by recycling of EOL PMs via Hydrogen Processing of Magnetic Scrap (HPMS) [21] or Selective Electrochemical Etching (SEE) [22].

[0006] CN104959618A discloses a core-shell structure Nd-Fe-B magnetic powder high in electrical resistivity and magnetic performance and application. The Strip Cast and Hydrogen decrepitated Nd-Fe-B powders are subjected to NH₃ gas (50-300 ml/min) at elevated tem-

peratures 300-400°C in between 5 and 30 min. Afterwards the powders are cooled down to room temperature. A core shell microstructure of the Nd₂Fe₁₄B matrix phase was developed, where the shell was a nitrided Nd₂Fe₁₄B phase. Such NH₃ modified materials exhibited enhanced properties with regards to electrical resistivity and corrosion performance, however the magnetic properties degraded upon nitriding. CN110853854 A describes a method to increase the anisotropy of main hard magnetic phase Nd₂Fe₁₄B phase in Nd-Fe-B permanent magnets, via diffusion of PrHoFe alloy and ZrCu alloy that is applied on the hydrogen crushed particles. US2006022175 A and US2006191601 A describe the formation of a fluorine-containing layer on the surface of the ferromagnetic (Nd-Fe-B) powder by using a solution containing at least one kind of alkaline earth element or rare-earth element, and fluorine. US2014291296 A discloses a method of producing nanoparticles by spark erosion and 1) coating the surface of the nanoparticles with smaller nanoparticles; or 2) forming an oxidized coating on the surface of the nanoparticles to produce core-shell surface oxidized nanoparticles. Implementations of the disclosed technology can produce permanent magnets that include Nd-Fe-B magnets further enhanced by addition of more expensive rare earth elements, e.g., such as Dy. For example, the disclosed spark erosion techniques can produce both Nd-Fe-B magnet alloy nanoparticles (e.g., less than 100 nm, and in some examples, less than 50 nm) and Dy or Dy-containing alloy nanoparticles of comparably or smaller size that are substantially free of surface oxide. None of these documents considers the coating of single crystalline magnetic particles from recycled EOL magnets that are obtained via hydrogen treatment or of single crystallites obtained via electrochemical etching. Kimura et al. [23] investigated the influence of Ta sputtering on the magnetic properties and microstructures of hydrogen crushed Nd-Fe-B powders with the aim of developing an improved method for fabricating anisotropic powders. However, the paper doesn't consider single crystalline magnetic particles from recycled EOL magnets that are obtained via hydrogen treatment or single crystallites obtained via electrochemical etching.

[0007] It is an object of the present invention to provide a method of forming a starting material for producing rare earth permanent magnets from recycled materials and a corresponding starting material, which allow the fabrication of high-performance Nd-Fe-B permanent magnets from end-of life Nd-Fe-B magnets and/or magnet scraps, in particular the fabrication of such magnets with improved corrosion resistance and increased energy density product by simultaneous increase of H_c and B_r.

Description of the Invention

[0008] The object is achieved with the method and starting material according to claims 1 and 9. Advantageous embodiments of the method and starting material

are subject of the dependent claims or can be derived from the subsequent portions of the description.

[0009] In a first step of the proposed method single $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains of end-of-life $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets and/or magnet scraps are provided. The single grains (single crystallites) are preferably obtained from the end-of-life $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets and/or magnet scraps by extracting the single grains via hydrogen or electrochemistry assisted methods, in particular by using selective electrochemical etching or hydrogen decrepitation. The provided single grains are then coated with a single layer or with a layer sequence of one or several grain boundary materials such that said single layer or layer sequence is covering each individual grain. The grain boundary material of said single layer or of the lowermost layer of said layer sequence is selected from one or several metals or metal compounds or alloys. The coated grains can then be condensed to bulk Nd-Fe-B permanent magnets, optionally via subsequent thermal treatments.

[0010] The coating of the grains is preferably performed with one or several of the following methods: chemical vapor deposition (CVD), physical vapor deposition (PVD), electroplating, electroless plating, electrophoretic deposition, powder blending, spray coating and sol-gel, the latter with the help of a solvent, which evaporates after the sol-gel coating procedure at room temperature or slightly elevated temperatures. The coating method may also depend on the grain boundary material to be coated.

[0011] Generally, the grain boundary material(s) in addition to the metals and alloys of lowermost layer, i.e. in other layers of the layer sequence, or as a closer specification of the metals and alloys of the single layer or lowermost layer (see (a) and (b)) may comprise any of the following components:

- (a) lanthanoid and transition metals and their alloys
- (b) metals that form alloys with lanthanoids and other transition metals, preferably elements from the rare earth elements group including light rare earths and heavy rare earths, together with the elements from the transition metals group of the periodic system. If using elements from the second group they have to wet the grain boundaries of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains, they can either form a eutectic alloy within the system of investigation (Nd-Fe-B) or they can be isomorphic forming solid solutions within the Nd-Fe-B system with the melting point T below the melting point of the $\text{Nd}_2\text{Fe}_{14}\text{B}$, but at the same time not forming any intermetallic or other phases with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, if magnets are to be consolidated via conventional liquid phase sintering.
- (c) metals that form alloys with lanthanoids and other transition metals, preferably elements from the rare earth elements group including light rare earths and heavy rare earths, together with the elements from the transition metals group of the periodic system. These metals need to fulfil the condition that they

have a melting point below the melting point of the $\text{Nd}_2\text{Fe}_{14}\text{B}$, but at the same time are not forming any intermetallic or other phases with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, if magnets are to be consolidated via sintering methods as spark plasma sintering.

(d) lanthanoid compositions with halogen elements and/or oxygen and/or carbon and/or nitrogen, e.g. lanthanoid oxides or fluorides; these materials serve as a source of lanthanoid metals upon heating and diffusion. Tb_3O_7 for example serves as a source for Tb metal, that diffuses into NdFeB. The same applies when using other metal compounds which form a source for the corresponding metal upon heating. The heating can be performed directly after applying the layer or during forming of the dense magnets.

(e) polymers

(f) ceramics

(g) glue

(h) resin

(i) amorphous materials like glasses

[0012] The grain boundary material of the single layer and of the lowermost or second layer (covering said lowermost layer) of the layer sequence is preferably selected from metals, metal compounds or alloys which are rare earth free or low in rare earth content. With this measure, we aim to reduce the total rare earth content of the PMs below the current ~32 wt.%. In the Nd-Fe-B PMs having GBs with low REE content we aim at total rare earth content of the PMs of preferably 29 wt.% and below. For the Nd-Fe-B PMs with GBs, not containing the REEs, we aim to total rare earth content of the PMs to equal the stoichiometry of $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase that equals to 26.7 wt. % of the REEs. Some, examples of appropriate metals or alloys for the grain boundary material are Nd-Cu, or Cu, Al-Cu-Zn or only Zn or Sn.

[0013] Preferably, the grain boundary material of said single layer or of at least one layer of said layer sequence is selected to have a lower melting point than the hard-magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and doesn't react with that phase. This enables the condensing of the coated grains to permanent magnets using thermal treatments without the need of any further binding material.

[0014] The single grains for the proposed method are preferably obtained via selective electrochemical etching or hydrogen decrepitation. In a preferred embodiment the selective electrochemical etching is performed by anodically oxidizing the $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets and/or magnet scraps using a non-aqueous liquid electrolyte. During the anodic oxidation the $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains in said $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets and/or magnet scraps released. The released $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains are collected magnetically during and/or after said anodic oxidation. Preferably the non-aqueous liquid electrolyte is formed of a transition metal-based salt in a non-aqueous bath.

[0015] In an alternative preferred embodiment the hydrogen decrepitation is performed by treating the

Nd₂Fe₁₄B magnets and/or magnet scraps with hydrogen gas. The hydrogen decrepitation releases a friable, demagnetised, hydrogenated powder from said Nd₂Fe₁₄B magnets and/or magnet scraps. The powder contains an interstitial hydride of Nd₂Fe₁₄BH_x (particles of 10 microns) and smaller particles (<1 micron) from the grain-boundary phase (NdH_{2.7}) of the magnets and/or magnet scraps.

[0016] The starting material according to the present invention is the result of the proposed method. The starting material comprises single Nd₂Fe₁₄B grains of end-of-life Nd₂Fe₁₄B magnets and/or magnet scraps, which grains are coated with a single layer or with a layer sequence of one or several grain boundary materials such that said single layer or layer sequence is covering each individual grain. The grain boundary material of the single layer or of the layers of the layer sequence is selected according to one or several embodiments of the above method.

[0017] With the proposed method and starting material novel bulk permanent magnets with increased properties and better corrosion resistance can be formed from end-of-life Nd-Fe-B magnets and/or magnet scraps using different kinds of densification methods. By starting from single Nd₂Fe₁₄B grains, first the Nd-rich grain boundary can be exchanged with a novel grain boundary phase (based on a low amount of REEs or based on compositions that don't contain any REEs) that is not prone to corrosion. In addition, starting from the single grains, the amount of the HREEs elements like Dy, can be finetuned to the ultimate concentration, that increases the coercivity (H_c) leaving the remanence (B_r) unaffected, that leads to an increased energy product (BH_{max}).

Brief description of the Figures

[0018] Embodiments of the invention will now be discussed with reference to the accompanying figures, which show:

Figure 1: Single Nd₂Fe₁₄B crystals obtained via hydrogen treatment (left), and via selective electrochemical etching (right).

Figure 2: A schematic diagram showing conventional sintering and annealing of Nd₂Fe₁₄B magnets (a), grain boundary diffusion of sintered magnets (b), and the formation of Nd₂Fe₁₄B magnets according to the present invention (c).

Embodiments of the Invention

[0019] The present invention suggests a new approach to increase the performance of Nd-Fe-B based permanent magnets: Single-crystal Nd₂Fe₁₄B particles recycled from end-of-life magnets are coated in nanometer- to micrometer thicknesses with grain boundary materials that are preferably either completely RE-free or much lower in RE-content than currently known grain

boundary phases, before producing the magnet. This allows much more efficient use of scarce heavy-REE materials like Dy or Tb, and also the introduction of completely new grain boundary phase materials in single-layer or multi-layer configurations, consisting of e.g. metals, alloys, polymers, ceramics or glasses (and combinations thereof), enabling to improve coercivity and remanence of the material at the same time. If single-crystal Nd₂Fe₁₄B matrix grains can be recovered by recycling of sintered magnets, grain smoothing processes have already happened during primary production, giving a new degree of freedom to use other materials as grain boundary phase to insulate the grains, and to tailor the magnetic properties during remanufacturing.

[0020] Such recovery is possible by Hydrogen Processing of Magnetic Scrap (HPMS)[21] and Selective Electrochemical Etching (SEE) [24]. With HPMS, on exposure to hydrogen the sintered Nd-Fe-B magnets break down into a friable, demagnetised, hydrogenated powder containing an interstitial hydride of Nd₂Fe₁₄BH_x (10 microns) and smaller particles (<1 micron) from the grain-boundary phase (NdH_{2.7}), as shown in *Figure 1*, left. The particle size corresponds to single-crystal Nd₂Fe₁₄B material (~10 μm), with agglomerates of Nd-rich phase/oxides particles, which are mechanically separated in an after-treatment process (e.g. in wind separators or magnetic separators). The SEE procedure is based on the electrochemical anodic etching of sintered Nd-Fe-B magnets in a non-aqueous dimethylformamide/FeCl₂ bath. Selective recovery of Nd₂Fe₁₄B grains is realized with application of current densities < 10 mA cm⁻². The etching priority of phases (metallic Nd > intergranular NdFe₄B₄ > matrix Nd₂Fe₁₄B) results in granular decomposition of the magnet, as shown in *Figure 1* (right). The Nd₂Fe₁₄B grains are then separated from the nonmagnetic grain-boundary phase (mainly consisting of Nd₂O₃, Dy₂O₃ and NdB₄). Starting with the RE₂Fe₁₄B grains that were recovered after the electrochemical selective leaching or the HPMS process to remove the Nd-rich phases and impurities, we are able to both minimize the amount of the grain-boundary phase that is introduced in a form of a sintering aid and tailor its chemical composition.

[0021] The removed Nd₂Fe₁₄B grains are preferably coated depending on the material

1. Via conventional powder blending techniques of powder metallurgy, here the elements from the rare earth elements group including light rare earths and heavy rare earths are selected (but not necessary), together with the elements from the transition metals group of the periodic system. The elements from the second group have to form an eutectic alloy within the system of investigation (Nd-Fe-B), need to have the melting T below the melting point of the Nd₂Fe₁₄B and don't react with the matrix phase Nd₂Fe₁₄B, for the conventional sintering approach.

2. Via conventional powder blending techniques of powder metallurgy, here the elements from 1. need

to fulfil the condition that they have a melting point below the melting point of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, but at the same time are not forming any intermetallic or other phases with the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase, if magnets are to be consolidated via sintering methods as spark plasma sintering.

3. Via chemical vapor deposition (CVD) and physical vapour deposition (PVD), here the elements from the group of rare earths, transition metals are considered as well as polymers.

4. Via electroless and electroplating, where the elements from the transition metals group of the periodic system are considered, as well as their alloys. Here the elements or and alloys have to form an eutectic alloy within the system of investigation (Nd-Fe-B) and don't react with the matrix phase $\text{Nd}_2\text{Fe}_{14}\text{B}$.

5. Via sol gel and electrophoretic deposition techniques here the elements forming glasses or ceramics are applied.

[0022] Figure 2 shows the concept of the invention in comparison to coating of the magnetic particles via state-of-the-art methods. State of the art approaches Fig. 2a and Fig. 2b show conventional sintering and annealing (a) and grain boundary diffusion of sintered magnets (b). In the conventional method of Fig. 2a $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains 1 with Nd-rich phase are mixed with Dy-rich particles 2 and then sintered and annealed to form the dense magnets. This results in corresponding Nd, Dy-rich grain boundaries 3. Using the technique of grain boundary diffusion of Fig. 2b, Dy, Tb elements 4 are added in small amounts on the surface of already sintered Nd-Fe-B magnets, where they are diffused along the Nd, Dy-rich grain boundaries 3 towards magnet interior substituting a part of Nd in the $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase and forming a Nd, Dy, Tb -rich grain boundary 5. The present invention is presented in scheme (c) by way of example - grain boundary engineering of recycled magnet powder. On the left side the recycled single crystalline powder particles 6 are presented that are coated in this example with metal elements (Element A, layer 7), e.g. lanthanoide elements and/or their alloys, and alloys (Element B, layer 8) with or without the lanthanoide elements. The binding for forming the dense magnets from the coated grains is done either via the grain material (A, B) of the lowermost two layers or via glasses or ceramics C or polymers D of one or several further layers. The coated single $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains 6 are then bonded by means of heat, pressure, evaporation of a solvent or a combination thereof to form a dense magnet. In this magnet the single grains 6 are separated by each other, as shown in Fig. 2c, by the coating 9 formed of the grain material of the lowermost two layers (A, B or AB) and by a coating 10 formed in this example by the ceramics C or polymers D. Generally, this further coating 10 may be formed of all

[0023] The right-hand side of Fig 2 shows a comparison of the HC-BR-diagrams of the magnets achieved with

the different methods, wherein the solid line refers to the method of Fig. 2a, the dashed line to the method of Fig. 2b and the dotted line to the method of Fig. 2c.

[0024] The rare earth recycled magnet starting material produced by the method of the invention can be used for forming dense magnets. The magnets are densified by liquefaction and subsequent hardening of at least one of the layers of the grain boundary phase. This can be achieved by all materials that are liquid at temperatures below the melting point of the $\text{Nd}_2\text{Fe}_{14}\text{B}$ hard-magnetic phase: metals with respective melting points, polymers, but also glue, resin, or amorphous materials with respective melting points like some glasses.

References:

[0025]

1. Sagawa, M., et al., Permanent magnet materials based on the rare earth-iron-boron tetragonal compounds. IEEE transactions on Magnetism, 1984. 20(5): p. 1584-1589.
2. Yang, Y., et al., REE recovery from end-of-life Nd-FeB permanent magnet scrap: a critical review Journal of Sustainable Metallurgy, 2017. 3(1): p. 122-149.
3. Betancourt, R.J.R.m.d.f., Nanocrystalline hard magnetic alloys. 2002. 48(4): p. 283-289.
4. Straumal, B., et al., Grain boundary wetting in the NdFeB-based hard magnetic alloys. Journal of Materials Science, 2012. 47(24): p. 8352-8359.
5. Hono, K. and H. Sepehri-Amin, Strategy for high-coercivity Nd-Fe-B magnets. Scripta Materialia, 2012. 67(6): p. 530-535.
6. Herbst, J., R 2 Fe 14 B materials: Intrinsic properties and technological aspects. Reviews of Modern Physics, 1991. 63(4): p. 819.
7. Nakamura, H., et al., Magnetic properties of extremely small Nd-Fe-B sintered magnets. IEEE transactions on magnetism, 2005. 41(10): p. 3844-3846.
8. Komatsu, T., et al. IUMRS-ICA 2008 Symposium'AA. Rare-Earth Related Material Processing and Functions'. in IOP Conference Series: Materials Science and Engineering. 2009. IOP Publishing.
9. Li, D., et al., Grain interface modification and magnetic properties of Nd-Fe-B sintered magnets. Japanese Journal of Applied Physics, 2008. 47(10R): p. 7876.
10. Zapf, L., et al. Proceedings of 20th international workshop on rare earth permanent magnet & their applications.
11. Soderznik, M., et al., The grain-boundary diffusion process in Nd-Fe-B sintered magnets based on the electrophoretic deposition of DyF_3 . Intermetallics, 2012. 23: p. 158-162.
12. Hirota, K., et al., Coercivity enhancement by the grain boundary diffusion process to Nd-Fe-B sin-

tered magnets. IEEE transactions on magnetics, 2006. 42(10): p. 2909-2911.

13. Löewe, K., et al., Temperature-dependent Dy diffusion processes in Nd-Fe-B permanent magnets. Acta Materialia, 2015. 83: p. 248-255.

14. Soderznik, M., et al., High-coercivity Nd-Fe-B magnets obtained with the electrophoretic deposition of submicron TbF₃ followed by the grain-boundary diffusion process. Acta Materialia, 2016. 115: p. 278-284.

15. Soderznik, M., et al., The grain-boundary diffusion process in Nd-Fe-B sintered magnets based on the electrophoretic deposition of DyF₃. Intermetallics, 2012. 23: p. 158-162.

16. McGuinness, P., et al., Replacement and Original Magnet Engineering Options (ROMEOS): A European Seventh Framework Project to Develop Advanced Permanent Magnets Without, or with Reduced Use of, Critical Raw Materials. JOM, 2015. 67(6): p. 1306-1317.

17. Gutfleisch, O., Controlling the properties of high energy density permanent magnetic materials by different processing routes. Journal of Physics D: Applied Physics, 2000. 33(17): p. R157.

18. Sepehri-Amin, H., et al., Grain boundary and interface chemistry of an Nd-Fe-B-based sintered magnet. Acta Materialia, 2012. 60(3): p. 819-830.

19. Matsuura, Y., et al., Phase diagram of the Nd-Fe-B ternary system. Japanese journal of applied physics, 1985. 24(8A): p. L635.

20. Fukagawa, T. and S. Hirose, Coercivity generation of surface Nd₂Fe₁₄B grains and mechanism of fcc-phase formation at the Nd/Nd₂Fe₁₄B interface in Nd-sputtered Nd-Fe-B sintered magnets. Journal of Applied Physics, 2008. 104(1): p. 013911.

21. Walton, A., et al., The use of hydrogen to separate and recycle neodymium-iron-boron-type magnets from electronic waste. Journal of Cleaner Production, 2015. 104: p. 236-241.

22. Xu, X., et al., Direct Recycling of Nd-Fe-B Magnets Based on the Recovery of Nd₂Fe₁₄B Grains by Acid-free Electrochemical Etching. ChemSusChem, 2019. 12(21): p. 4754-4758.

23. Kimura, M., et al., Fabrication of Anisotropic Nd-Fe-B Powders by Ta Sputtering. Materials transactions, 2019. 60(5): p. 830-836.

24. Xu, X., et al., Direct Recycling of Nd-Fe-B Magnets Based on the Recovery of Nd₂Fe₁₄B Grains by Acid-free Electrochemical Etching. 2019. 12(21): p. 4754-4758.

Claims

1. A method of forming a starting material for producing rare earth permanent magnets from recycled materials, at least comprising the following steps:

- providing single Nd₂Fe₁₄B grains (6) of end-of-life Nd₂Fe₁₄B magnets and/or magnet scraps, and

- coating the grains (6) with a single layer or with a layer sequence (7, 8, 10) of one or several grain boundary materials such that said single layer or layer sequence (7, 8, 10) is covering each individual grain (6),

wherein the grain boundary material of said single layer or of a lowermost layer (7) of said layer sequence (7, 8, 10) is selected from one or several metals or metal compounds or alloys.

2. The method according to claim 1, wherein the coating of the grains (6) is performed with any of the following methods: blending, chemical vapor deposition (CVD), physical vapor deposition (PVD), electroplating, electroless plating, electrophoretic deposition, powder blending, spray coating and sol-gel.

3. The method according to claim 1 or 2, wherein the grain boundary material of said single layer or of at least one layer of said layer sequence (7, 8, 10) is selected to have a lower melting point than the hard-magnetic Nd₂Fe₁₄B phase.

4. The method according to any one of claims 1 to 3, wherein the grain boundary material of said single layer is selected from metals or metal compounds or alloys which metals, metal compounds or alloys are rare earth free or low in rare earth content.

5. The method according to any one of claims 1 to 3, wherein the grain boundary material of said lowermost layer (7) of said layer sequence (7, 8, 10) is selected from heavy rare earth elements or their alloys or compounds.

6. The method according to claim 5, wherein the grain boundary material of a second layer (8) covering said lowermost layer (7) in said layer sequence (7, 8, 10) is selected from metals or metal compounds or alloys which metals, metal compounds or alloys are rare earth free or low in rare earth content.

7. The method according to any one of claims 1 to 3, 5 and 6, wherein the grain boundary material of at least one further layer (10) of said layer sequence (7, 8, 10) is selected from any one of the following material groups: polymers, ceramics, glue, resin and amorphous materials like glasses.

8. The method according to any one of claims 1 to 7, wherein the step of providing single Nd₂Fe₁₄B grains

(6) of end-of-life $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets and/or magnet scraps includes the step of recovering the grains (6) from the end-of-life $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets and/or magnet scraps using selective electrochemical etching or hydrogen decrepitation.

5

or a combination thereof to form a magnetic structure, wherein the single grains of the hard magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase are separated by each other in this structure with a grain boundary phase formed by the grain boundary material(s).

9. A starting material for forming rare earth permanent magnets, comprising single $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains (6) of end-of-life $\text{Nd}_2\text{Fe}_{14}\text{B}$ magnets and/or magnet scraps, said grains being coated with a single layer or with a layer sequence (7, 8, 10) of one or several grain boundary materials such that said single layer or layer sequence (7, 8, 10) is covering each individual grain (6), wherein the grain boundary material of said single layer or of layers of said layer sequence (7, 8, 10) is selected according to the method of one or several of the preceding claims.

10

15

20

10. The starting material according to claim 9, wherein the layer sequence comprises

--- a first lanthanoid rich layer (7) as said lowermost layer, formed directly on a surface of each individual grain (6);

25

--- a second layer (8) based on lanthanoides and/or other metals and/or their alloys,

--- at least one further layer (10) formed on the second layer (8).

30

11. The starting material according to claim 9, wherein the layer sequence comprises

--- a first layer (8) based on lanthanoides and/or other metals and/or their alloys as said lowermost layer, formed directly on a surface of each individual grain (6); and

35

--- at least one further layer (10) formed on the first layer (8).

40

12. The starting material according to claim 10 or 11, wherein said at least one further layer (10) is formed of any one of the following material groups: polymers, ceramics, glue, resin and amorphous materials like glasses.

45

13. The starting material according to any one of claims 9 to 12, wherein the grain boundary material of said single layer or of at least one layer of said layer sequence (7, 8, 10) is selected to have a lower melting point than the hard-magnetic $\text{Nd}_2\text{Fe}_{14}\text{B}$ phase.

50

14. Use of the starting material according to any one of claims 9 to 13 for forming dense magnets, wherein the coated single $\text{Nd}_2\text{Fe}_{14}\text{B}$ grains (6) are bonded by means of heat, pressure, evaporation of a solvent

55

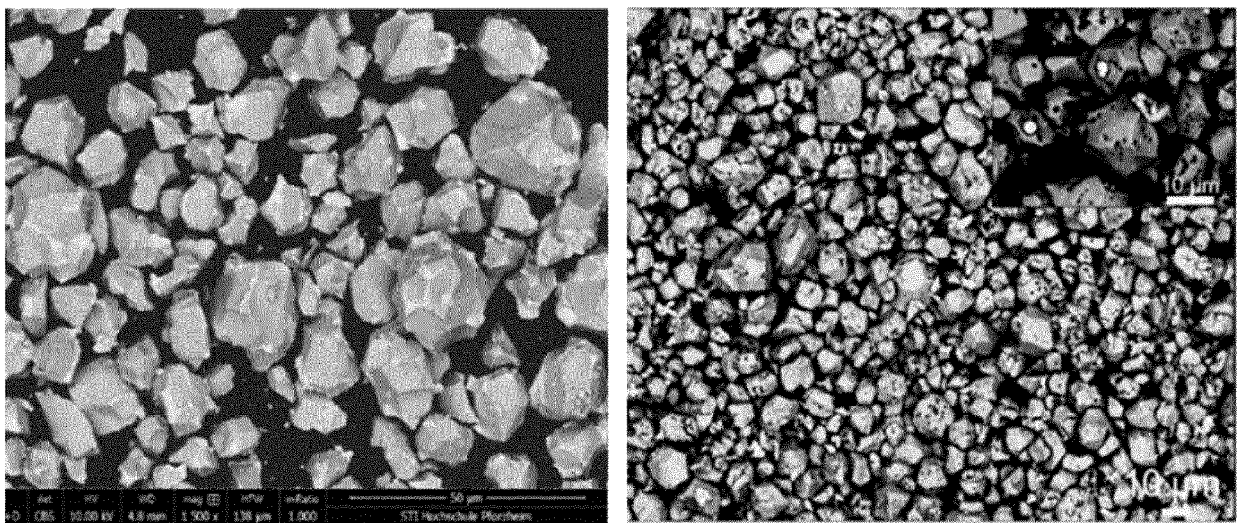


Fig. 1

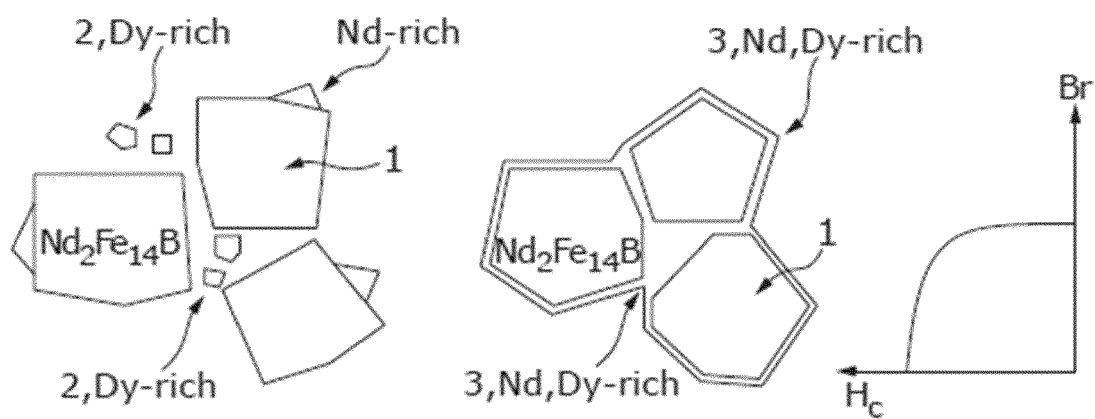


Fig. 2a

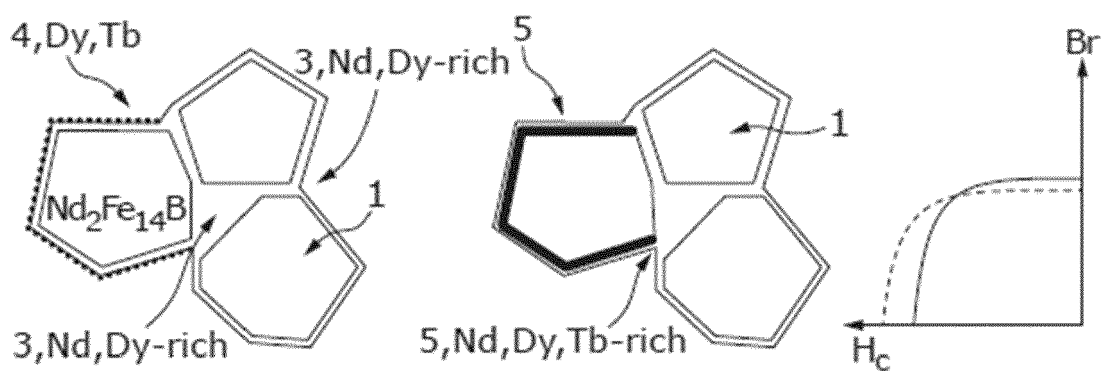


Fig. 2b

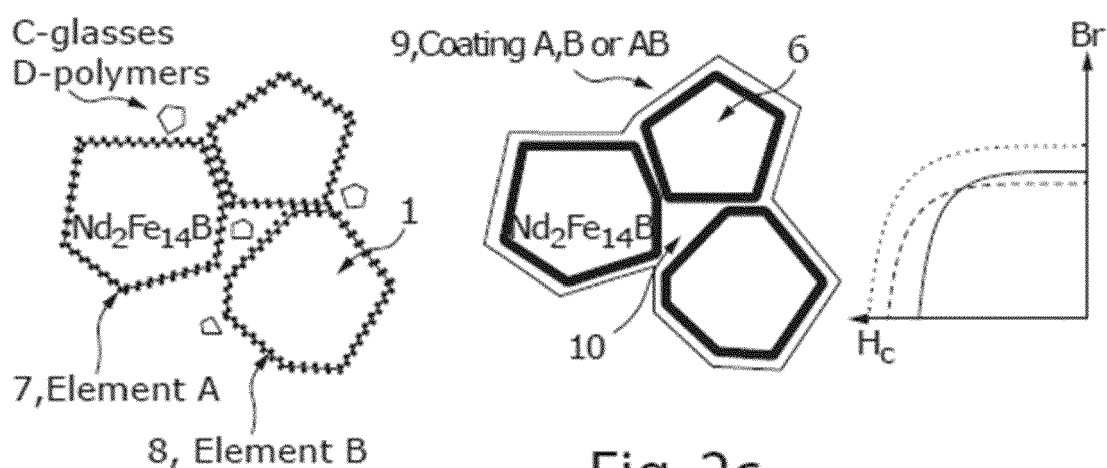


Fig. 2c



EUROPEAN SEARCH REPORT

Application Number
EP 21 16 5521

5

10

15

20

25

30

35

40

45

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	CN 104 036 944 A (UNIV BEIJING TECHNOLOGY) 10 September 2014 (2014-09-10) * abstract; claim 1 * * title *	1-4,8,9, 13,14 5-7, 10-12	INV. B22F1/00 B22F1/02 B22F8/00 B22F9/02 C22C38/00 C23C16/00 C30B29/52 H01F1/057 H01F41/02 C22B7/00 C22B59/00
Y	JP 2020 521339 A (GRIREM ADVANCED MATERIALS CO.,LTD) 16 July 2020 (2020-07-16) * paragraphs [0008], [0022]; claims 1-2; figure 1 *	5-7, 10-12	
Y	FR 3 069 096 A1 (COMMISSARIAT ENERGIE ATOMIQUE [FR]) 18 January 2019 (2019-01-18) * claims 1-5; example 1 *	6,10	ADD. B22F9/00
Y	CN 112 375 914 A (WEIFANG JIUTIAN STRONG MAGNETIC CO LTD) 19 February 2021 (2021-02-19) * claims 1-10 *	5-7, 10-12	
A,D	US 2006/191601 A1 (KOMURO MATAHIRO [JP] ET AL) 31 August 2006 (2006-08-31) * paragraphs [0019], [0031] *	1-14	TECHNICAL FIELDS SEARCHED (IPC)
A	WO 2017/132075 A1 (URBAN MINING COMPANY [US]) 3 August 2017 (2017-08-03) * paragraphs [0120], [0130]; figure 1 *	9-13	B22F C30B C23C C22C H01F C21C C22B
A	US 2015/294787 A1 (ZLATKOV BRANISLAV [AT]) 15 October 2015 (2015-10-15) * paragraphs [0002], [0014], [0025], [0029], [0034], [0049], [0052], [0055]; claims 1,2,3,4,8; figures 2-3 *	9,14	
A	US 2014/366687 A1 (ZAKOTNIK MIHA [US] ET AL) 18 December 2014 (2014-12-18) * paragraphs [0068] - [0069]; figure 5; example 1 *	1-8	
The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 20 September 2021	Examiner Aliouane, Nadir
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

EPO FORM 1503 03.82 (P04C01)

50

55

ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.

EP 21 16 5521

5

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on

The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

20-09-2021

10

15

20

25

30

35

40

45

50

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 104036944 A	10-09-2014	NONE	
JP 2020521339 A	16-07-2020	CN 109841367 A DE 112018001808 T5 JP 6799196 B2 JP 2020521339 A US 2021151226 A1 WO 2019105013 A1	04-06-2019 19-12-2019 09-12-2020 16-07-2020 20-05-2021 06-06-2019
FR 3069096 A1	18-01-2019	NONE	
CN 112375914 A	19-02-2021	NONE	
US 2006191601 A1	31-08-2006	CN 1825737 A CN 101908808 A JP 4591112 B2 JP 2006238604 A US 2006191601 A1	30-08-2006 08-12-2010 01-12-2010 07-09-2006 31-08-2006
WO 2017132075 A1	03-08-2017	EP 3408044 A1 JP 2019511133 A TW 201739929 A US 2019051434 A1 WO 2017132075 A1	05-12-2018 18-04-2019 16-11-2017 14-02-2019 03-08-2017
US 2015294787 A1	15-10-2015	CN 104919546 A DE 102013004985 A1 EP 2920796 A1 KR 20150086311 A US 2015294787 A1 WO 2014075890 A1	16-09-2015 15-05-2014 23-09-2015 27-07-2015 15-10-2015 22-05-2014
US 2014366687 A1	18-12-2014	AU 2014281646 A1 BR 112015031725 A2 CN 105723480 A EP 3011573 A2 EP 3790029 A1 HK 1222472 A1 JP 6312821 B2 JP 2016532287 A JP 2018157212 A JP 2020047926 A TW 201517075 A US 2014366687 A1 US 2014369881 A1 US 2015068030 A1	11-02-2016 25-07-2017 29-06-2016 27-04-2016 10-03-2021 30-06-2017 18-04-2018 13-10-2016 04-10-2018 26-03-2020 01-05-2015 18-12-2014 18-12-2014 12-03-2015

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

55

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- CN 104959618 A [0006]
- CN 110853854 A [0006]
- US 2006022175 A [0006]
- US 2006191601 A [0006]
- US 2014291296 A [0006]

Non-patent literature cited in the description

- **SAGAWA, M. et al.** Permanent magnet materials based on the rare earth-iron-boron tetragonal compounds. *IEEE transactions on Magnetism*, 1984, vol. 20 (5), 1584-1589 [0025]
- **YANG, Y. et al.** REE recovery from end-of-life NdFeB permanent magnet scrap: a critical review. *Journal of Sustainable Metallurgy*, 2017, vol. 3 (1), 122-149 [0025]
- **BETANCOURT, R.J.R.M.D.F.** Nanocrystalline hard magnetic alloys, 2002, vol. 48 (4), 283-289 [0025]
- **STRAUMAL, B. et al.** Grain boundary wetting in the NdFeB-based hard magnetic alloys. *Journal of Materials Science*, 2012, vol. 47 (24), 8352-8359 [0025]
- **HONO, K. ; H. SEPEHRI-AMIN.** Strategy for high-coercivity Nd-Fe-B magnets. *Scripta Materialia*, 2012, vol. 67 (6), 530-535 [0025]
- **HERBST, J. R** 2 Fe 14 B materials: Intrinsic properties and technological aspects. *Reviews of Modern Physics*, 1991, vol. 63 (4), 819 [0025]
- **NAKAMURA, H. et al.** Magnetic properties of extremely small Nd-Fe-B sintered magnets. *IEEE transactions on magnetism*, 2005, vol. 41 (10), 3844-3846 [0025]
- IUMRS-ICA 2008 Symposium'AA. Rare-Earth Related Material Processing and Functions. **KOMATSU, T. et al.** IOP Conference Series: Materials Science and Engineering. IOP Publishing, 2009 [0025]
- **LI, D. et al.** Grain interface modification and magnetic properties of Nd-Fe-B sintered magnets. *Japanese Journal of Applied Physics*, 2008, vol. 47 (10R), 7876 [0025]
- **ZAPF, L. et al.** *Proceedings of 20th international workshop on rare earth permanent magnet & their applications* [0025]
- **SODERŽNIK, M. et al.** The grain-boundary diffusion process in Nd-Fe-B sintered magnets based on the electrophoretic deposition of DyF₃. *Intermetallics*, 2012, vol. 23, 158-162 [0025]
- **HIROTA, K. et al.** Coercivity enhancement by the grain boundary diffusion process to Nd-Fe-B sintered magnets. *IEEE transactions on magnetism*, 2006, vol. 42 (10), 2909-2911 [0025]
- **LÖEWE, K. et al.** Temperature-dependent Dy diffusion processes in Nd-Fe-B permanent magnets. *Acta Materialia*, 2015, vol. 83, 248-255 [0025]
- **SODERŽNIK, M. et al.** High-coercivity Nd-Fe-B magnets obtained with the electrophoretic deposition of submicron TbF₃ followed by the grain-boundary diffusion process. *Acta Materialia*, 2016, vol. 115, 278-284 [0025]
- **SODERŽNIK, M. et al.** The grain-boundary diffusion process in Nd-Fe-B sintered magnets based on the electrophoretic deposition of DyF₃. *Intermetallics*, 2012, vol. 23, 158-162 [0025]
- **MCGUINNESS, P. et al.** Replacement and Original Magnet Engineering Options (ROMEOS): A European Seventh Framework Project to Develop Advanced Permanent Magnets Without, or with Reduced Use of, Critical Raw Materials. *JOM*, 2015, vol. 67 (6), 1306-1317 [0025]
- **GUTFLEISCH, O.** Controlling the properties of high energy density permanent magnetic materials by different processing routes. *Journal of Physics D: Applied Physics*, 2000, vol. 33 (17), R157 [0025]
- **SEPEHRI-AMIN, H. et al.** Grain boundary and interface chemistry of an Nd-Fe-B-based sintered magnet. *Acta Materialia*, 2012, vol. 60 (3), 819-830 [0025]
- **MATSUURA, Y. et al.** Phase diagram of the Nd-Fe-B ternary system. *Japanese journal of applied physics*, 1985, vol. 24 (8A), L635 [0025]
- **FUKAGAWA, T. ; S. HIROSAWA.** Coercivity generation of surface Nd₂Fe₁₄B grains and mechanism of fcc-phase formation at the Nd/Nd₂Fe₁₄B interface in Nd-sputtered Nd-Fe-B sintered magnets. *Journal of Applied Physics*, 2008, vol. 104 (1), 013911 [0025]
- **WALTON, A. et al.** The use of hydrogen to separate and recycle neodymium-iron-boron-type magnets from electronic waste. *Journal of Cleaner Production*, 2015, vol. 104, 236-241 [0025]
- **XU, X. et al.** Direct Recycling of Nd-Fe-B Magnets Based on the Recovery of Nd₂Fe₁₄B Grains by Acid-free Electrochemical Etching. *ChemSusChem*, 2019, vol. 12 (21), 4754-4758 [0025]

- **KIMURA, M. et al.** Fabrication of Anisotropic Nd-Fe-B Powders by Ta Sputtering. *Materials transactions*, 2019, vol. 60 (5), 830-836 **[0025]**
- **XU, X. et al.** *Direct Recycling of Nd-Fe-B Magnets Based on the Recovery of Nd₂Fe₁₄B Grains by Acid-free Electrochemical Etching*, 2019, vol. 12 (21), 4754-4758 **[0025]**