



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

(43) Date of publication:
16.11.2016 Bulletin 2016/46

(21) Application number: **14876586.0**

(22) Date of filing: **29.12.2014**

(51) Int Cl.:
H01F 1/055 ^(2006.01) **C22C 1/04** ^(2006.01)
C22C 19/00 ^(2006.01) **C22C 33/02** ^(2006.01)
C22C 38/00 ^(2006.01)

(86) International application number:
PCT/ES2014/000223

(87) International publication number:
WO 2015/101682 (09.07.2015 Gazette 2015/27)

(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

(30) Priority: **30.12.2013 ES 201400015**

(71) Applicants:
• **Universidad De Sevilla**
41013 Sevilla (ES)
• **Universidad De Huelva**
21071 Huelva (ES)

(72) Inventors:
• **MONTES MARTOS, Juan Manuel**
Sevilla (ES)
• **CINTAS FÍSICO, Jesús**
E-41092 Sevilla (ES)
• **GÓMEZ CUEVAS, Francisco**
E-21071 Huelva (ES)
• **TERNERO FERNÁNDEZ, Fátima**
E-41092 Sevilla (ES)

(74) Representative: **Pons**
Glorieta Ruben Dario 4
28010 Madrid (ES)

(54) **METHOD FOR PRODUCING MAGNETS USING POWDER METALLURGY**

(57) The invention relates to a novel method for producing magnets (especially applicable to the production of magnets containing rare earths). The novelty of the method lies in its use of a type of electrical consolidation (such as so-called electrical resistance sintering, ERS, or so-called electrical discharge consolidation, EDC, but not necessarily one of the these) as a substitute for the conventional cold pressing and sintering method which is usually used. The method according to the invention achieves: (1) combining the compacting/sintering steps, significantly cutting the duration thereof and reducing the magnitude of the working pressures; (2) implementing the steps of magnetic aligning, pressing/sintering, heat treatment and magnetising in the same matrix; and (3) rendering superfluous the use of protective atmospheres during the sintering process.

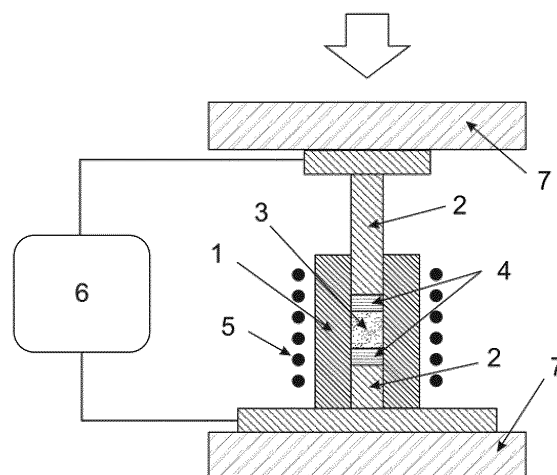


Figure 1

Description

OBJECT OF THE INVENTION

[0001] This technical invention corresponds to the technical scientific area of "materials technology" and the sector of activity to which it would be applied is the manufacture of permanent magnets from powders.

[0002] The object of this patent is to demonstrate an alternative method for manufacturing magnets, indicated especially for those which include rare earths in their composition, which do not modify the magnetic processes, but do modify the processes relating to the forming, replacing the conventional method (cold pressing followed by sintering in a furnace) with a new consolidation method consisting of any rapid consolidation method, electrical or technical, FAST (field assisted sintering technique), from which notable advantages are derived: greater brevity, joining the pressing/sintering processes into one single step, use of low pressures, absence of controlled atmospheres and possibility of implementing magnetic alignment processes, pressing/sintering, heat treatment and magnetization, the powder remaining in the same die. All of which is designed to mainly achieve a significant reduction of the manufacturing cost of the magnet.

STATE OF THE ART

[0003] Unlike soft magnetic materials, *magnets* are hard magnetic materials which are not easily demagnetized once they have been magnetized, thus providing a technologically utilizable, stable magnetic field, which is not affected by external magnetic fields. Magnets are characterized by a high coercive field (coercivity) and high remanent induction (remanence) which is also translated into a high-energy product [J.W. Fiepk, Permanent Magnet Materials, "Properties and Selection: Nonferrous Alloys and Special-Purpose Materials", Vol 2, ASM Handbooks, ASM International, 1990, p. 782-803]. Such characteristics are achieved with a meticulous manufacturing process. The process is even more elaborate if the magnet contains rare earths. The development of these types of magnets was started at the beginning of the 1960s when Nesbitt and Wernicke [(E.A. Nesbitt, H.J. Williams, J.H. Wernicke, R.C. Sherwood, J. Appl. Phys., Vol 32S, 1961, p 342-343); (E.A. Nesbitt, H.J. Williams, J.H. Wernicke, R.C. Sherwood, J. Appl. Phys., Vol 33, 1962, p 1674-1678); (J.H. Wernicke, S. Geller, Acta Cryst., Vol 12, 1959, p 662-665)] established the structure, magnetic moment and Curie temperature of the intermetallic compounds of cobalt/rare earths.

[0004] The conventional process for manufacturing magnets (for example those which contain rare earths) proceeds from a powder with a high intrinsic crystalline anisotropy (for example due to a crystalline structure with a hexagonal cell), a very specific composition and very particular grain size (the average size of the particles

should be comparable to the critical diameter of a mono-domain particle, between 1 and 10 μm and also the size distribution should be very narrow [(K.H. Moyer, Magnetic Materials and Properties for Powder Metallurgy Part Applications, "Powder Metal Technologies and Applications", Vol 7, ASM Handbook, ASM International, 1998, 1006-1020); (N.A. Spaldin, "Magnetic Materials: Fundamentals and Applications", 2nd edition, Cambridge University Press, 2011, USA, 3-144].

[0005] This powder, or a mixture of different types of these, is exposed to a strong magnetic field ($\sim 2\text{-}5\text{ MA/m}$) with the aim of forcing the magnetic alignment of the particles which constitute it (forcing, for example, the c axis of the hexagonal cells of the mono-crystalline particles to be preferably parallel to the direction of the applied field); thus the magnetization of the final piece can be the highest possible [F.V. Lenel, "Powder Metallurgy: Principles and Applications", Metal Powder Industries Federation, Princeton, NJ, 1980, p. 531-548]].

[0006] After this magnetic alignment process, the aligned powder is subjected to cold pressing (with pressures which fluctuate between 700 and 1500 MPa) with the aim of compacting it. This compaction process can be carried out in different ways: by cold die pressing (CDP) or by cold isostatic pressing (CIP). When the pressing is carried out in a die, the powder can remain confined in the same die during the alignment and compaction steps. When the pressing is isostatic, the pressing system imposes limitation, which forces the alignment to be carried out prior to the introduction into the press, normally confining it to a plastic container. Although in theory, if the method selected is die pressing, the magnetic alignment can be carried out in the same compaction die, the high pressures used require very large dies which move the magnetic coil away from the powder, reducing the magnetic field applied. If the alignment is carried out independently, the coil can be closer to the powder and apply larger fields which improve the alignment grade of the particles and thus the magnetic properties of the final pieces. This is generally the reason why the alignment and the pressing are developed in different dies [(J.W. Fiepk, Permanent Magnet Materials, "Properties and Selection: Nonferrous Alloys and Special-Purpose Materials", Vol 2, ASM Handbooks, ASM International, 1990, p. 782-803); (K.H. Moyer, Magnetic Materials and Properties for Powder Metallurgy Part Applications, "Powder Metal Technologies and Applications", Vol 7, ASM Handbook, ASM International, 1998, 1006-1020); F.V. Lenel, "Powder Metallurgy: Principles and Applications", Metal Powder Industries Federation, Princeton, NJ, 1980, p. 531-548]].

[0007] After the compaction process, the pieces obtained can reach a relative density of the order of 80%. These green compacts are then sintered in a furnace, in suitable atmosphere (usually argon) at temperatures which are around 1100° C. After the sintering, the relative density can increase to approximately 90%.

[0008] Although less common, the powders can also

be hot formed by means of the hot isostatic pressing (HIP) technique. The pressing and sintering steps are thus combined, but not the alignment process which should continue to be carried out independently [J.W. Fiepe, Permanent Magnet Materials, "Properties and Selection: Nonferrous Alloys and Special-Purpose Materials", Vol 2, ASM Handbooks, ASM International, 1990, p. 782-803]. The main drawback with this technique is its high cost and its low production level.

[0009] After sintering, it is common to apply some heat treatment (around 900° C) intended to improve the coercivity of the material. Said heat treatments generally strive for the nucleation, fixing and anchoring of the walls of the magnetic domains on the surfaces and grain limits of the material which substantially increases the coercive force [K.H. Moyer, Magnetic Materials and Properties for Powder Metallurgy Part Applications, "Powder Metal Technologies and Applications", Vol 7, ASM Handbook, ASM International, 1998, 1006-1020].

[0010] Lastly, the pieces are magnetized by again applying an intense magnetic field (of 5 MA/m). Due to the high remanence and high coercivity of some types of magnets processed in this way, the magnetization process can end up being quite difficult. It is often more efficient to magnetize by means of applying short-duration, but more intense, pulses which has been revealed as an effective technique for moving and pulling the walls of the magnetic domains, thus enabling the increase of the magnetization.

[0011] Possibly after this treatment, some pieces (especially those which have iron among their components) should be coated with the aim of improving their resistance to corrosion. The coating methods can be very diverse [(J.W. Fiepe, Permanent Magnet Materials, "Properties and Selection: Nonferrous Alloys and Special-Purpose Materials", Vol 2, ASM Handbooks, ASM International, 1990, p. 782-803); (K.H. Moyer, Magnetic Materials and Properties for Powder Metallurgy Part Applications, "Powder Metal Technologies and Applications", Vol 7, ASM Handbook, ASM International, 1998, 1006-1020)], those which should be cited include, as examples, galvanizing and chromium plating.

[0012] Even when the current powder metallurgical technology for manufacturing permanent magnets can be considered satisfactory in many senses, certain improvements would be desirable, aimed at simplifying the process and which significantly reduce the production costs. The manufacturing technique proposed in this patent application strives to meet this challenge.

DESCRIPTION OF THE INVENTION

[0013] The object of the present invention is a method for the powder-metallurgical manufacture of magnets which comprises, as the initial step, the introduction of a powdery material which contains at least one magnetic element selected from Fe, Co, Ni into a die; once the powdery material has been introduced into the die, it is

sequentially and always subjected to magnetic alignment; electrical consolidation process, heat treatment, cooling and magnetization in the same die.

[0014] In a particular embodiment, the powdery material also contains at least one element of the elements known as rare earths.

[0015] In further preferred embodiments, the powdery material is mixed with at least one second powdery material with a different composition and which comprises at least one first element which is selected from Fe, Co, Ni. This second powdery material can comprise at least one second element which is selected from among the elements known as rare earths.

[0016] The options for putting the steps constituting the method into practice are stated below:

- 1) The magnetic alignment is carried out by exposing the powdery material to the action of a magnetic field.
- 2) The electrical consolidation process can be executed:

- by means of the electrical resistance sintering technique, particularly medium frequency.
- by means of the electrical discharge consolidation technique.
- by means of sequentially applying the electrical discharge consolidation technique and electrical resistance sintering technique or in reverse, firstly

sintering and then discharging.

3) The heat treatment of the material subsequent to the electrical consolidation is carried out by means of the passage of electric current through the material.

4) The cooling step after the heat treatment is carried out by contact with the cooled electrodes by means of a cooling liquid.

5) The magnetization step of the material is effected by the action of a magnetic field which allows the magnetic saturation of the material to be reached.

[0017] Optionally, the steps are carried out in controlled atmospheric conditions, particularly in inert gas atmosphere or in a vacuum.

DESCRIPTION OF THE FIGURE

[0018] **Figure 1:** Diagram of the equipment proposed for the manufacture of powder metallurgical magnets by electrical consolidation. There is one die containing the powder and the powder is magnetically aligned therein, electrically consolidated, possibly heat-treated and lastly magnetized.

DESCRIPTION OF THE INVENTION

[0019] The manufacture of magnets (especially those

which contain rare earth elements) is a complex, multi-step task which includes both magnetic processes (magnetic alignment of particles and magnetization of the final piece) and forming processes (cold pressing, sintering and heat treatments), some of which require rigorous control of the atmosphere used in order to prevent undesirable contaminations. Due to the high cost of the primary material (the rare earths are expensive) and due to its complex manufacturing process, the final cost of these magnets is very high, and prohibitive in many cases for certain applications.

[0020] The object of the invention is a method for the powder-metallurgical manufacture of magnets, indicated especially for those which include rare earths in their composition, which do not modify the magnetic processes, but do modify the processes relating to the forming, replacing the conventional method (cold pressing followed by sintering in a furnace) with a new consolidation method consisting of any rapid consolidation method, electrical or technical, FAST (field assisted sintering technique), from which notable advantages are derived: greater brevity, joining the pressing/sintering processes into one single step, use of low pressures, absence of controlled atmospheres and possibility of implementing magnetic alignment processes, pressing/sintering, heat treatment and magnetization, the powder remaining in the same die. All of which is designed to mainly achieve a significant reduction of the manufacturing cost of the magnet.

[0021] The object of the present invention is to present a novel method for manufacturing magnets (especially applicable to the manufacture of magnets which contain rare earths). The novelty of the method lies in the use of electrical consolidation techniques (like the technique called electrical resistance sintering (ERS) or the technique called electrical discharge consolidation (EDC) which are mentioned for illustrative, non-limiting purposes) in lieu of the conventional cold pressing + sintering method commonly used. This achieves: (1) combining the compaction/sintering steps, significantly shortening their duration and reducing the magnitude of the working pressures, (2) carrying out the steps of magnetic alignment, pressing/sintering, heat treatment and magnetization in the same die and (3) rendering the use of protective atmospheres during the sintering process unnecessary.

[0022] The electrical consolidation techniques (those known generally as FAST techniques not only allow the steps of cold pressing and sintering in a furnace to be combined into one single step, but also for their duration to be reduced such that it renders the use of inert atmospheres unnecessary (the time in which the powder is exposed to the high temperatures is too brief for the undesirable oxidation reactions to take place) and the process can be carried out in the open. The reduction of the time can end up being very significant: if the entire process of cold pressing (die or isostatic) and sintering in a furnace can take around 30-60 minutes, the electrical consolidation can be carried out in only a few seconds or even less

time, depending on the specific method used. By way of example, it should be said that the two previously mentioned methods, ERS and EDC, have characteristic durations of around seconds and milliseconds, respectively, and electrical power sources that are also different: in ERS, a transformer which provides low voltage, ~ 10V and high intensity, ~ 5 - 20 kA and in EDC, a capacitor bank capable of supplying, during the discharge thereof, voltages of ~ 50 - 300 V and intensities of 1 - 5 kA. ERS can use low-frequency electric current (50 Hz) or medium-frequency, around 1000 Hz.

[0023] Given that the electrical consolidation techniques are basically a certain type of hot pressing, much lower working pressures (< 100 MPa) are required than those used in cold pressing of the conventional method (between 700 and 1500 MPa). In this way, with the electrical consolidation, the dies can have considerably thinner walls, which also makes it possible for the coil used for the magnetic alignment and possibly the magnetization to adhere more to the powder, allowing it to not only receive a more intense magnetic field, but also to be able to be magnetically aligned in the same die where it will subsequently be consolidated, heat-treated and possibly also magnetized.

[0024] The heat treatment prior to the final magnetization can be carried out by the passage of an electric current through the material, with an intensity such that it causes the required heating of the piece by means of the Joule effect. Generally, the value of this intensity will be less than that used during the consolidation step. The cooling will be carried out owing to the cooling system which the frames of the machines should have in contact with the electrodes/punches. In order to carry out this step, atmosphere controlled by means of suitable experimental regulation could possibly be used.

[0025] A diagram of the electrical consolidation equipment, especially in relation to the details of the die is shown in Figure 1, which presents, for illustrative, non-limiting purposes:

- The die is electrically isolating, for example, manufactured with natural rock, refractory concrete, ceramic tube and metal beam, etc.
- The electrodes will be made of any copper alloy with high conductivity, for example Cu-Zr alloy. In order to achieve greater uniformity in the interior temperature, it may be interesting to interpose between the powder and the electrode a somewhat less conductive wafer material, for example a Cu-W pseudo alloy (heavy metal) which also provides resistance to electrical erosion.
- In the case of ERS, the power source can consist of a welding transformer which provides current intensities in the range of 2 to 12 kA, whether with grid frequencies of 50 Hz or better still, with greater frequencies, in the range of average frequencies of around 1000 Hz. A second possibility in the case of EDC could consist of the use of a capacitor bank

with a high capacity and load voltages in the range of 50 to 500 V as the power source. Another possibility is to operate both types of sources, for example in a sequential application of the same: first discharge by capacitors, then actuate the welding transformer. This last possibility may have the advantage of being able to handle larger pieces, the electrical resistance of which is too high to be handled only by means of the ERS technique.

- The mechanical device which exerts the pressure should be capable of supplying the force required for reaching pressures of around 100 MPa.
- The coil which envelopes the die will be connected to an additional power source which can benefit from the methods commonly used for such purpose, for example, magnetization by impulses, which is mentioned for illustrative, but non-limiting purposes. This coil will be responsible for applying the magnetic field for aligning particles and magnetizing the already consolidated piece.

EMBODIMENT OF THE INVENTION

[0026] As an illustrative example of the novelty of the invention, the manufacture of a specific type of magnetic will be analyzed below, one of the magnets called cobalt/rare earth magnets, with a nominal SmCo_5 composition, (a) by means of the conventional method (currently followed by the industry) and (b) by means of the method proposed by this patent application.

[0027] The powders from which the method proceeds require the same characteristics one way or another. Thus, the two first steps are common:

1. Two powders, with a medium particle size of 6 to 8 μm and very narrow grain size distribution and one of these with a composition of 33.8% Sm - 66.2% Co by weight (nominally SmCo_5), and the other with a composition of 60% Sm - 40% Co by weight.
2. The pertinent quantities of one powder and another are taken such that the average composition is 62.6% Co (by weight). These two powders are mixed by agitation, obtaining a composition with slightly less cobalt than the nominal stoichiometry of the SmCo_5 compound.

Conventional method

[0028]

3. The powder mixture is enclosed in a plastic cover and subjected to magnetic alignment by the action of a magnetic field of the order of 5 MA/m.
4. The magnetically aligned powder mixture is brought to an isostatic press where it is compacted at the approximate pressure of 1400 MPa in order to obtain a density of 6.9 g/cm^3 , which represents approximately 80% of the absolute value of the den-

sity of the compound.

5. The green compact obtained in the previous step is sintered in a furnace, under a purified argon atmosphere, at a temperature of between 1090 and 1150° C for a time of around 40 minutes. The compact densifies until reaching a density of 7.7 g/cm^3 , which represents approximately 90% of the absolute density.

6. After sintering in the furnace, the piece is subjected to a heat treatment at 900° C for 15 minutes, with the aim of improving the coercive force.

7. The compacts are lastly magnetized in a field of ~ 5 MA/m.

8. The magnet is possibly coated in order to reinforce its resistance to corrosion.

Method object of the present invention

[0029] A diagram of the equipment required could be that indicated in Figure 1.

[0030] The die 1 is electrically isolating (for example manufactured with natural rock, refractory concrete, ceramic tube and metal beam, etc.).

[0031] The electrodes 2 will be made of any copper alloy with high conductivity (for example, Cu-Zr alloy). In order to achieve greater uniformity in the interior temperature, it may be interesting to interpose between the powder 3 and the electrode 2 a somewhat less conductive wafer material 4, for example a Cu-W pseudo alloy (heavy metal) which also provides resistance to electrical erosion.

[0032] The coil 5 is responsible both for carrying out the magnetic alignment process and the final magnetization process.

[0033] The power source 6 can consist of a welding transformer (in the case of ERS) or a capacitor bank (in the case of EDC). Another possibility is to operate both types of sources, for example in a sequential application of the same: first discharge by capacitors, and then intervention of the welding transformer.

[0034] The mechanical device 7 which exerts the pressure should be capable of supplying the force required for achieving pressures to guarantee the desired densification level.

3. The powder mixture is introduced into the die of the ERS consolidation equipment and is magnetically aligned there by the action of a magnetic field of the order of 5 MA/m.

4. The electrical consolidation process by ERS is initiated, in the open, with nominal parameters of 80 MPa of pressure, a current density of -6.5 kA/cm^2 and a period of time of 70 cycles of 0.02 s per cycle. The final density of the compact is 90% or greater.

5. With the sinterization concluded and without removing the compact from the ERS equipment, a current density of around 1 - 2 kA/cm^2 is made to pass for periods of time which fluctuate between 400 cy-

cles (8 seconds). A smooth heat treatment is thus effected. The compact is cooled in-situ by the effect of the electrodes which are cooled by water.

6. With the heat treatment finished, the compact is magnetized without leaving the die by the action of a magnetic field with a value of ~5 MA/m.

7. The magnet is possibly coated in order to reinforce its resistance to corrosion.

[0035] The maximum remanences, coercivities and energy products achieved by means of both ways are 1.0 T, 3024 kA/m and 605 kT A/m, respectively. The conventional data have been taken from Lenel [F.V. Lenel, "Powder Metallurgy: Principles and Applications", Metal Powder Industries Federation, Princeton, NJ, 1980, p. 531-548].

Claims

1. A method for the powder-metallurgical manufacture of magnets which comprises, as initial step, the introduction of a powdery material, which contains at least one magnetic element selected from Fe, Co, Ni, into a die, **characterized in that** once the powdery material has been introduced into the die, it is sequentially subjected to the following, always in the same die:

- magnetic alignment;
- electrical consolidation process;
- heat treatment;
- cooling, and
- magnetization.

2. The method according to claim 1, **characterized in that** the powdery material also contains at least one element from the elements known as rare earths.

3. The method according to any one of claims 1 to 2, **characterized in that** prior to the introduction into the die, the powdery material is mixed with at least one second powdery material of a different composition and which comprises at least one first element which is selected from Fe, Co, Ni.

4. The method according to claim 3, **characterized in that** the second powdery material comprises at least one second element which is selected from the elements known as rare earths.

5. The method according to any one of claims 1 to 4, **characterized in that** the magnetic alignment step is carried out by exposing the powdery material to the action of a magnetic field.

6. The method according to any one of claims 1 to 5, **characterized in that** the electrical consolidation

process is carried out by means of the electrical resistance sintering technique.

7. The method according to claim 6, **characterized in that** the electrical consolidation process is carried out by means of the medium-frequency electrical resistance sintering technique.

8. The method according to any one of claims 1 to 5, **characterized in that** the electrical consolidation process is carried out by means of the electrical discharge consolidation technique.

9. The method according to any one of claims 1 to 8, **characterized in that** the electrical consolidation process is carried out by means of sequentially applying the electrical discharge consolidation and electrical resistance sintering techniques.

10. The method according to any one of claims 1 to 8, **characterized in that** the electrical consolidation process is carried out by means of sequentially applying the electrical resistance sintering and electrical discharge consolidation techniques.

11. The method according to any one of claims 1 to 10, **characterized in that** the heat treatment of the material subsequent to the electrical consolidation is carried out by means of the passage of electric current through the material.

12. The method according to any one of claims 1 to 11, **characterized in that** the cooling of the material after the heat treatment is carried out by contact with the electrodes cooled by means of a cooling liquid.

13. The method according to any of claims 1 to 12, **characterized in that** the step of magnetizing the material is carried out by the action of a magnetic field which allows the magnetic saturation of the material to be reached.

14. The method according to any one of claims 1 to 13, **characterized in that** the steps are carried out in controlled atmospheric conditions.

15. The method according to claim 14, **characterized in that** the steps are carried out in an inert gas atmosphere or in a vacuum.

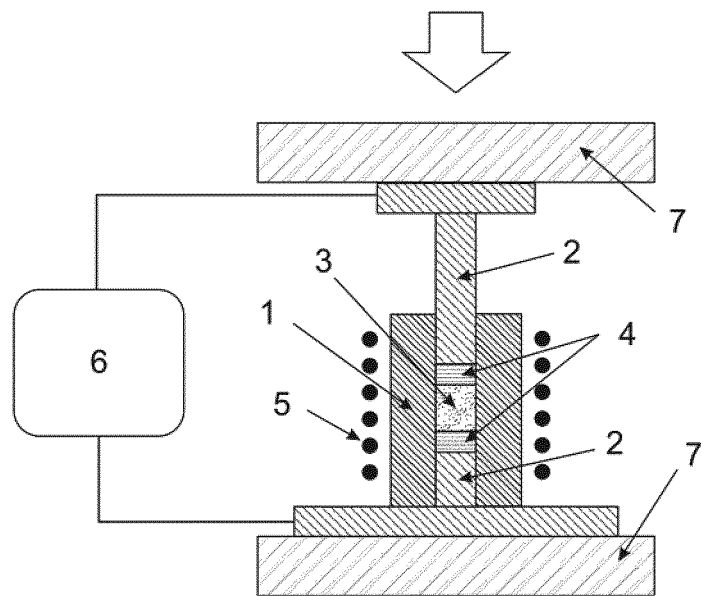


Figure 1

INTERNATIONAL SEARCH REPORT

International application No.
PCT/ES2014/000223

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

H01F, C22C

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)

EPODOC, INVENES, WPI, TXT

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0029071 A1 (NAMIKI PRECISION JEWEL CO LTD) 27/05/1981, abstract; example 5, claims 1-3.	1-15
Y		1-5,12-15
Y	US 5382303 A (ANDERSON RICHARD L ET AL.) 17/01/1995, columns 8 - 10; 12.	1-15
Y		1-5,12-15
Y	Fabricación pulvimetalúrgica de núcleos magnéticos 13/05/2013, [on line][retrieved on 10/03/2015]. Retrieved from Internet: <URL:http://otri.us.es/otri/documentacion/Patentes /Folleto%20JD_069_201201228_Ternero_2013-05-13.pdf>	1-15
Y	OFFER from Spain, reference: TOES20130719004, Powder-metallurgy based fabrication of magnetic nuclei, 19/07/2013, [on line], [retrieved on 9/03/2015]. Retrieved from Internet: <URL:http://www.enterpriseeuropenetwork.nl/totpublic/print/1398343>	1-5,12-15

☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:	"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
"A" document defining the general state of the art which is not considered to be of particular relevance.	
"E" earlier document 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)	"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
"O" document referring to an oral disclosure use, exhibition, or other means.	"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 documents, such combination being obvious to a person skilled in the art
"P" document published prior to the international filing date but later than the priority date claimed	"&" document member of the same patent family

Date of the actual completion of the international search
11/03/2015

Date of mailing of the international search report
(16/03/2015)

Name and mailing address of the ISA/

Authorized officer
M. García Poza

OFICINA ESPAÑOLA DE PATENTES Y MARCAS
Paseo de la Castellana, 75 - 28071 Madrid (España)
Facsimile No.: 91 349 53 04

Telephone No. 91 3495568

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/ES2014/000223

C (continuation).	DOCUMENTS CONSIDERED TO BE RELEVANT	
Category *	Citation of documents, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2013266473 A1 (WANG YUCONG) 10/10/2013, abstract; paragraphs [0003]; [0007 - 0009]; [0020]; [0023 - 0024]; claims 1-3; 12, 19.	1-5,12-15
A	US 4221613 A (IMAZUMI NOBUO ET AL.) 09/09/1980.	1-15
A	EP 2527062 A1 (TDK CORP) 28/11/2012.	1-15
A	EP 0156483 A1 (SHERRITT GORDON MINES LTD) 02/10/1985.	1-15

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/ES2014/000223

Information on patent family members

Patent document cited in the search report	Publication date	Patent family member(s)	Publication date
EP0029071 A1	27.05.1981	US4369075 A JPS5625941 A WO8002297 A1 JPS55140203 A	18.01.1983 12.03.1981 30.10.1980 01.11.1980
US5382303 A	17.01.1995	US5781843 A	14.07.1998
US2013266473 A1	10.10.2013	JP2013219353 A CN103366941 A DE102013205769 A1	24.10.2013 23.10.2013 10.10.2013
US4221613 A	09.09.1980	USRE31317E E JPS54104408 A	19.07.1983 16.08.1979
EP2527062 A1	28.11.2012	US2008053273 A1 US7858023 B2 JP2006265643 A JP4666145B B2 JP2006128598 A JP4282025B B2 WO2006003872 A1 JP2006100597 A JP4282017B B2 JP2006100432 A JP4282015B B2 JP2006016645 A JP4057563B B2 JP2006016644 A JP4057562B B2 JP2006019382 A JP4282013B B2 JP2006016642 A JP4057561B B2 EP1762316 A1 EP1762316 A4 CN1938115 A CN1938115B B	06.03.2008 28.12.2010 05.10.2006 06.04.2011 18.05.2006 17.06.2009 12.01.2006 13.04.2006 17.06.2009 13.04.2006 17.06.2009 19.01.2006 05.03.2008 19.01.2006 05.03.2008 19.01.2006 17.06.2009 19.01.2006 05.03.2008 14.03.2007 08.06.2011 28.03.2007 12.05.2010
EP0156483 A1	02.10.1985	US4746378 A JPS60238463 A JPH0515775B B2 EP0156482 A1 EP0156482 B1 CA1237965 A1 AT43363T T	24.05.1988 27.11.1985 02.03.1993 02.10.1985 24.05.1989 14.06.1988 15.06.1989

Form PCT/ISA/210 (patent family annex) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/ES2014/000223

5
10
15
20
25
30
35
40
45
50
55

CLASSIFICATION OF SUBJECT MATTER

H01F1/055 (2006.01)
C22C1/04 (2006.01)
C22C19/00 (2006.01)
C22C33/02 (2006.01)
C22C38/00 (2006.01)

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.

Non-patent literature cited in the description

- Permanent Magnet Materials, "Properties and Selection: Nonferrous Alloys and Special-Purpose Materials. **J.W. FIEPKE**. ASM Handbooks. ASM International, 1990, vol. 2, 782-803 [0003] [0006] [0008] [0011]
- **E.A. NESBITT ; H.J. WILLIAMS ; J.H. WERNICKE ; R.C. SHERWOOD**. *J. Appl. Phys.*, 1961, vol. 32S, 342-343 [0003]
- **E.A. NESBITT ; H.J. WILLIAMS ; J.H. WERNICKE ; R.C. SHERWOOD**. *J. Appl. Phys.*, 1962, vol. 33, 1674-1678 [0003]
- **J.H. WERNICKE ; S. GELLER**. *Acta Cryst.*, 1959, vol. 12, 662-665 [0003]
- Magnetic Materials and Properties for Powder Metallurgy Part Applications, "Powder Metal Technologies and Applications. **K.H. MOYER**. ASM Handbook. ASM International, 1998, vol. 7, 1006-1020 [0004] [0006] [0009] [0011]
- **N.A. SPALDIN**. Magnetic Materials: Fundamentals and Applications. Cambridge University Press, 2011, 3-144 [0004]
- **F.V. LENEL**. Powder Metallurgy: Principles and Applications. *Metal Powder Industries Federation*, 1980, 531-548 [0005] [0006] [0035]