(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 2 123 781 A1**

(12) # EUROPEAN PATENT APPLICATION

(43) Date of publication:
25.11.2009 Bulletin 2009/48

(21) Application number: **08155922.1**

(22) Date of filing: **08.05.2008**

(51) Int Cl.:
C22C 1/00 (2006.01) *C22C 33/00* (2006.01)
C22C 33/04 (2006.01) *C22C 33/06* (2006.01)
C22C 45/00 (2006.01) *C22C 45/02* (2006.01)
C22C 45/04 (2006.01)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT RO SE SI SK TR
Designated Extension States:
AL BA MK RS

(71) Applicant: **OCAS N.V. - Onderzoekscentrum voor Aanwending van Staal**
9060 Zelzate (BE)

(72) Inventors:
- **Ruiz Romera, Daniel**
9060 Zelzate (BE)
- **Claessens, Serge**
9060 Zelzate (BE)
- **De Wulf, Marc**
9060 Zelzate (BE)
- **Van Steenberge, Nele**
9060 Zelzate (BE)
- **Antonissen, Joachim**
9060 Zelzate (BE)

(74) Representative: **pronovem**
Office Van Malderen
Avenue Josse Goffin 158
1082 Bruxelles (BE)

(54) **Amorphous alloy and method for producing products made thereof**

(57) The present invention is related to amorphous metallic product, formed of an alloy having a chemical formula of

$$Fe_{100-a-b-c-d-x-y}\, M_aNb_bSi_cB_dI_xJ_y$$

wherein :
- M is Co and/or Ni,
- I is one or more elements of the group consisting of Al, Cr, Cu, Mn, C and P,
- J is one or more elements of the group consisting of Ti, S, N and O

and wherein a, b, c, d, x and y are satisfying the following conditions : 0wt.%≤a≤46.1wt.%, 5.4wt.%≤b≤12.4wt.%, 2.2wt.%≤c≤4.4wt.%, 2wt.%≤d≤6wt.%, x≤2wt.% and y≤0.2wt.%. The invention is particularly related to a ring core for differential switchgears. The invention is equally related to a process for producing a product according to the invention.

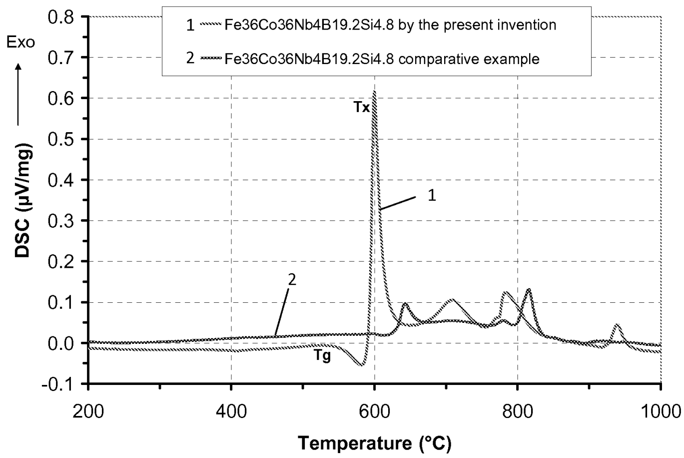

Fig. 1

EP 2 123 781 A1

Description

Field of the Invention

[0001] The present invention is related to products produced from Fe-based amorphous alloys (also called bulk metallic glass), and to the application of such products, in particular as magnetic cores.

State of the art.

[0002] The production of Fe-based bulk metallic glass (BMG) is difficult due to the low glass forming ability shown by known Fe-alloys used for this purpose, in comparison for example to Zr-based alloys. For this reason, a large number of elements are usually added to Fe in order to produce Fe-based BMG's. With 'bulk' we refer to three-dimensional bodies, wherein the smallest dimension is at least 0.3mm.

[0003] Besides the need for a large number of elements (minimum 4), the number of impurities must be carefully controlled in order to avoid crystallization by heterogeneous nucleation during casting. This demands the use of very pure base elements which are in fact very expensive making the current production processes of Fe-based BMG's very costly. Some impurities can cause in addition a decrease in the final aimed properties; therefore their levels must be carefully controlled. Fe-based amorphous materials generally have good soft magnetic properties, i.e. coercivity is very low and permeability shows large values. The FeNbBSi-alloy is a known example in terms of these characteristics. It is known in the art to fabricate ribbons of these compositions and also to apply such ribbons for making magnetic cores. The ribbons (20μm) are wound to form a ring-shaped product. Other techniques involve the cutting of "thick" ribbons (up to 50μm) with a ring-shape and the stacking of them in order to form the thick ring-core. All these steps make the production of such magnetic cores more expensive.

[0004] Also, some bulk metallic glass products, such as products obtained from sintered powders, are not suitable for low frequency (e.g. 50Hz or 60Hz) applications. **T**here is currently no soft magnetic amorphous Fe-based material having a thickness higher than 300μm with a high level of impurities (industrial ferroalloys used) and suitable for soft magnetic applications.

Aims of the invention

[0005] The present invention aims to provide an amorphous Fe-based alloy and a process for producing products made thereof, said alloy and products being producable from industrial base materials, whilst yielding an end product with soft magnetic properties and being suitable for low frequency applications.

Summary of the invention

[0006] The invention is related to a product and process, as disclosed in the appended claims. Preferred embodiments are disclosed in combinations of the independent claims with one or more claims dependent thereon.

[0007] In particular, the present invention is related to amorphous metallic product, formed of an alloy having a chemical formula of

$$Fe_{100-a-b-c-d-x-y}\ M_aNb_bSi_cB_dI_xJ_y$$

wherein :

- M is Co and/or Ni,
- I is one or more elements of the group consisting of Al, Cr, Cu, Mn, C and P,
- J is one or more elements of the group consisting of Ti, S, N and O

  and wherein a, b, c, d, x and y are satisfying the following conditions : 0wt.%≤a≤46.1wt.%, 5.4wt.%≤b≤12.4wt.%, 2.2wt.%≤c≤4.4wt.%, 2wt.%≤d≤6wt.%, x≤2wt.% and y≤0.2wt.%. The invention is particularly related to a ring core for differential switchgears. The invention is equally related to a process for producing a product according to the invention.

Brief description of the figures

[0008] Figure 1 illustrates the DSC of an amorphous rod (2mm) $Fe_{36}CO_{36}Nb_4B_{19.2}Si_{4.8}$ produced with raw Fe-alloys and following the present invention (curve 1). As a comparison an example of the same composition but not amorphous is shown (curve 2). In the latter example, the O-content in the master alloys exceeded the recommended limit, O > 300 ppm.

[0009] Figure 2 shows the XRD spectrum of an amorphous rod (2mm) of $Fe_{36}CO_{36}Nb_4B_{19.2}Si_{4.8}$ produced with raw Fe-alloys according to the present invention.
[0010] Figure 3 shows the B-H loop of a $Fe_{36}CO_{36}Nb_4B_{19.2}Si_{4.8}$ amorphous rod of 2 mm diameter.

Detailed description of the invention

[0011] The invention is related to an amorphous Fe-alloy having the chemical formula of $Fe_{100-a-b-c-d-x-y}M_aNb_bSi_cB_dI_xJ_y$ wherein :

- M is Co and/or Ni,
- I is one or more elements of the group consisting of Al, Cr, Cu, Mn, C and P,
- J is one or more elements of the group consisting of Ti, S, N and O
- and wherein a, b, c, d, x and y are satisfying the following conditions : 0wt.%≤a≤46.1wt.%, 5.4wt.%≤b≤12.4wt.%, 2.2wt.%≤c≤4.4wt.%, 2wt.%≤d≤6wt.%, x≤2wt.% and y≤0.2wt.%.

[0012] Alternatively, when the ranges of M, Nb, Si and B are expressed in at.%, a, b, c, d, are satisfying the following conditions : 0at.%≤a≤36at.%, 3at.%≤b≤6at.%, 4at.%≤c≤7at.%, 10at.%≤d≤25at.%, with x≤1.8at.% and y≤0.15at.%. According to a preferred embodiment, 0.05≤x≤2wt.% and 0.01≤y≤0.2wt.%. According to another embodiment, x≤1wt.% and/or y≤0.1wt.%. According to a further embodiment, 0.05≤x≤1wt.%. When M is both Co and Ni, the formula should be interpreted as $Fe_{100-a-b-c-d-x-y}Co_{a'}Ni_{a''}Nb_bSi_cB_dI_xJ_y$ with a'+a'' = a. When the alloy comprises oxygen, the O-content is preferably lower than or equal to 0.05wt%.
[0013] The invention is thus related to any product, and in particular to a bulk metallic product, formed of the alloy of the invention. With 'bulk metallic product' is meant a product with the smallest dimension (e.g. thickness in case of a cylinder-like rod) of higher than 300μm. According to a preferred embodiment of such a product, a ring-core for a differential switchgear is provided. The thickness of said ring core is at least 300μm, preferably at least 1mm. The properties of a product according to the invention, such as a ring core are :

- coercivity between 0.5A/m and 10A/m, and
- relative magnetic permeability between 50000 and 500000.

The ring cores according to the invention are suitable for low frequency applications (50Hz or 60Hz).

[0014] The invention is equally related to a process for producing an amorphous metal product having a composition according to the alloy of the invention. The process of the invention starts from starting materials which comprise Fe-containing alloys, i.e. non-pure materials. The starting materials may comprise raw Fe-alloys used in the steel industry. These materials are introduced into a melting device, and heated up to a temperature higher than their melting temperature, preferably between 1300°C and 1600°C. In the case for example of the $Fe_{36}CO_{36}Nb_4B_{19.2}Si_{4.8}$ composition it is preferred to have a temperature higher than 1350°C. The melting can be done under air or under a protective atmosphere, e.g. Ar. The use of a controlled atmosphere with low oxygen level can favour the cleanness of the resulting product (i.e. a low level of impurities and oxygen). According to a preferred embodiment, the atmosphere is controlled by creating a vacuum in the melting chamber before introducing the starting materials. In this case, before melting, a vacuum of at least 10^{-1} bar, preferably at least 10^{-2} bar, is created inside the chamber in order to get a clean atmosphere. During melting, an Ar-atmosphere can be used, for example at a pressure of 1 bar.
[0015] The material is kept in a molten state during a period of time, preferably between 100s and 300s, to promote homogenization (especially important for the dissolution of FeB). Then the molten material is cast into a mould, preferably a Cu-mould, and cooled down to form the product.
[0016] According to a preferred embodiment, the starting materials are one or more of the following : electrolytic-Fe, AK-steel (Al-killed steel), FeB, FeSi, FeNb and pure Co. The alloys FeB, FeSi and FeNb are materials used by the steel industry, which may comprise other elements than expressed by the alloy formula.
In the context of this invention, the composition of the starting materials is defined by the limits expressed in table 1 (all values in wt%).

Table 1 : composition of starting materials

	Electrolytic-Fe	Ak-steel	FeB	FeSi	FeNb	Pure Co
C	0.0005-0.1	0.0005-0.1	0.01-0.5	0.001-0.3	0.001-0.3	-
Mn	0.0001-0.2	0.001-0.5	0.01-2	0.01-1	0.01-1	-
Si	0.0001-0.1	0.0001-0.3	0.01-2	62-75	0.2-3	-

(continued)

	Electrolytic-Fe	Ak-steel	FeB	FeSi	FeNb	Pure Co
P	0.0005-0.03	0.0005-0.1	0.0005-0.1	0.0005-0.1	0.0005-0.1	-
S	0.0001-0.05	0.0005-0.01	0.0005-0.1	0.0005-0.1	0.0005-0.2	-
Al	0.0001-0.2	0.0001-0.4	0.001-0.8	0.001-0.8	0.001-1.2	-
Ti	0.0001-0.1	0.0001-0.1	0.0001-1	0.0001-1	0.0001-1	-
Nb	0.0001-0.1	0.0001-0.1	0.0001-0.1	0.0001-0.1	60-74	-
Cu	0.0001-0.08	0.001-0.1	0.001-0.3	0.001-0.1	0.001-0.3	-
Cr	0.0001-0.08	0.001-0.1	0.001-0.5	0.001-0.1	0.001-0.1	-
Ni	0.0001-0.08	0.001-0.1	0.001-0.3	0.001-0.1	0.001-0.1	-
As	0.0001-0.02	0.0001-0.05	0.0001-0.1	0.0001-0.05	0.0001-0.05	-
Sn	0.0001-0.02	0.0001-0.05	0.0001-0.1	0.0001-0.05	0.0001-0.05	-
O	0.001-0.1	0.0005-0.1	0.002-0.1	0.001-0.05	0.001-0.05	-
N	0.0003-0.01	0.0005-0.02	0.0005-0.05	0.0005-0.02	0.0005-0.02	-
B	0.0001-0.001	0.0001-0.001	15-21	0.0001-0.001	0.0001-0.001	-
Mo	0.0001-0.05	0.001-0.1	0.001-0.3	0.001-0.1	0.001-0.1	-
Zr	0.001-0.05	0.001-0.08	0.001-0.2	0.001-0.1	0.001-0.1	-
V	0.0001-0.1	0.0001-0.1	0.0001-0.5	0.0001-0.3	0.0001-0.3	-
Co	0.0001-0.1	0.0001-0.1	0.0001-0.1	0.0001-0.1	0.0001-0.1	99.5-99.95
Fe	Rest	Rest	78.3	22.9	28.9	-

[0017] The total amount of impurities in the Fe-alloys used as starting materials for the production of soft magnetic bulk according to the invention is preferably lower than 4% and more preferably lower than 2%. With impurities is meant the elements that are not nominally present in the alloy. For example, Nb is an impurity in FeB. Moreover, the amount of Mn in the Fe-alloys (starting materials) is preferably lower than 2% and more preferably lower than 1%.

[0018] The melting step can be performed in a levitation melter, e.g. a 100cc levitation melter. A levitation melter is a cold crucible induction melter. It consists of a copper crucible cooled by a circulation of water and a coil system creating a varying magnetic field. This magnetic field creates Foucault currents in the conductive materials inside the crucible which have three effects : heating the metals in the crucible up to their melting point, stirring the molten alloy, thus homogenising it, and making the molten mass levitate. During levitation melting, there is no contact between the molten alloy and the crucible, which can remain cold while the melt can stay clean.

[0019] When a levitation melter of 100kW power is used for the realization of the process of the invention, it is preferred to melt the materials at a power of at least 25% of the total power and preferably in the range 25-50% of the total power. When the melting takes place under protective atmosphere, the pressure in the melting chamber is preferably at least 1 atm.

[0020] According to an embodiment, the steps of the process as described above are used to form a master alloy. These steps are then followed by a further series of steps to form the final product, e.g. a ring core. It is important to have in the master alloy an O-level lower than 0.05 wt.% and it is preferred that this level is lower than 0.03 wt.%.

[0021] For a good magnetic performance, some impurities must not exceed certain values in the master alloy or final product : Ti, S and N. The total amount of (Ti + S + N) must be lower than 0.2% and preferably lower than 0.1%. On the other hand, other impurities might reach higher values, being beneficial for the glass forming ability. This is the case of Al, Ni, Cr, Cu, Mn, C and P.

However, when a certain value is exceeded, the properties of the material can be damaged. This value can be fixed to 2% and preferably to 1%.

[0022] The further steps of producing the bulk metallic glass product from the master alloy can be done in a melting device, like an induction melting device or a levitation melting device. An air atmosphere can be used although a controlled atmosphere or an atmosphere with low oxygen levels is preferable. The BMG can be cast in rods of up to 4mm, but also in other shapes, like ring-cores.

[0023] The process to form the BMG-product from the master alloy preferably comprises the following steps :

- A piece of master alloy is introduced in the melting device. The melting device can be a levitation melter of 12kW. An air atmosphere can be used although it is preferable to use of a controlled atmosphere like for example an Ar-atmosphere.
- Heating up the master alloy up to a temperature higher than its melting temperature. This temperature is in the case of FeCoNbBSi alloy higher than 1250°C. When a 12kW levitation melter is used, a minimum power of 50% must be used and preferably a power of at least 60% should be used. The material must be molten for at least 5 seconds and preferably during a time longer than 10 seconds. The heating up to the melting temperature can be done with only one ramp, but it can be preferably done in several heating steps. For example when a 12kW levitation melter is used, the following heating cycle can be used: 5 seconds at 20% of the power, 5 seconds at 35 % of the power, 5 seconds at 50% of the power and 2 seconds at 60% of the total power.
- Pouring the material into a Cu-mould at a temperature higher than the melting, but preferably not exceeding by more than 20 °C the melting temperature when the aimed diameter is between 2 and 3 mm. It is preferred to pour the material at a "low" temperature in order to prevent crystallization.
- Cooling the molten material, to obtain the product.

Examples - test results

[0024] The following table 2 gives an example of the composition of starting materials used in the method of the invention (in wt.%).

Table 2

	Electrolytic-Fe	Ak-steel	FeB	FeSi	FeNb	Pure Co
C	0.0013	0.0010	0.2	0.008	0.017	-
Mn	0.0001	0.0500	0.48	0.063	0.21	-
Si	0.0005	-	1.10	66.9	1.83	-
P	0.0010	0.0030	0.001	0.001	0.10	-
S	0.0001	0.0030	0.001	0.001	0.042	-
Al	0.0001	0.0030	0.10	0.025	0.60	-
Ti	-	-	0.026	0.073	0.35	-
Nb	-	-	-	-	63.3	-
Cu	0.0005	0.0080	0.11	0.004	0.04	-
Cr	0.0001	0.0150	0.19	0.009	0.02	-
Ni	0.0002	0.0100	0.12	0.007	0.01	-
As	0.0001	-	-	-	-	-
Sn	0.0001	-	-	-	-	-
O	0.0245	0.0050	0.0220	0.029	0.074	-
N	0.0008	0.0028	0.005	0.004	0.004	-
B	0.0001	-	18.6	-	-	-
Mo	-	0.0010	-	-	-	-
Zr	-	-	-	-	-	-
V	-	-	-	-	-	-
Co	-	-	-	-	-	99.9
Fe	Rest	Rest	78.3	22.9	28.9	-

[0025] The amorphicity of the obtained materials can be tested by means of different techniques. DSC (differential scanning calorimetry) and XRD are two known examples. Differential scanning calorimetry gives the evolution of heat capacity of a sample when it is heated. The sample is heated along with a reference (an empty crucible) so that both always have similar temperatures, controlled with accuracy. The difference between the energies brought to the sample and reference to heat them up at the same rate is monitored and gives the difference of behaviour. Endothermic and exothermic transformations in the sample can be spotted because they happen when respectively more or less energy must be brought to it to keep the same heating rate. So changes in heat capacity indicate phase transitions such as crystallisation or even simple transformations like glass transition.

[0026] Figure 1 gives the DSC of an $Fe_{36}Co_{36}Nb_4B_{19.2}Si_{4.8}$ alloy produced according to the method of the invention. A glass transition and a first crystallization peak are clearly visible on the figure (curve 1). On the other hand, the curve 2 on the DSC curve has no visible glass transition and a very slight crystallisation peak at around 600. This means that the sample is not fully amorphous and contains only a very small amount of amorphous phase. During the production of this comparison example (curve 2), it was detected that the oxygen of the master alloy was over the recommended limits, being higher than 300 ppm. For this reason it was not possible to produce a bulk metallic glass.

[0027] Like all amorphous materials (e.g. polymers, silica-based glasses) and unlike crystalline material, bulk metallic glass shows no peak of diffraction on an X-ray diffractogram but a broad halo. This is due to the lack of long-range order and crystallinity and to the presence of short range order. The X-ray diffraction diagram of an amorphous sample with chemical composition $Fe_{36}CO_{36}Nb_4B_{19.2}Si_{4.8}$ produced according to the present invention is shown by figure 2, where no Bragg peaks can be noticed, meaning that the sample is essentially amorphous.

[0028] The magnetic properties of the materials produced according to the present invention have been tested, see figure 3. Figure 3 shows the B-H loop of $Fe_{36}Co_{36}Nb_4B_{19.2}Si_{4.8}$ as measured by means of a Vibrating Sample Magnetometer (VSM). A saturation magnetization of 1.04T is measured together with a coercivity of 4.5A/m.

[0029] A hysteresis loop tracer was used to measure systematically the coercivity of the bulk metallic glass products produced according to the present invention. Table 3 presents the results corresponding to two materials from the present invention and two comparative examples. The measurements were performed on 2 mm diameter rods of as-cast materials; no additional annealing treatments have been performed. The bulk metallic glasses show very low values of coercivity, making these materials very suitable for soft magnetic applications. On the other hand, when the material is only partially amorphous the coercivity reaches very high values. In this comparative example, the O-content of the master alloy exceeded the limits of the present invention (>300ppm). For this reason it was not feasible to produce a bulk metallic glass with such master alloy. The second comparative example corresponds to a bulk metallic glass product of the same composition but prepared with pure elements. The amorphous materials produced by the present invention, i.e. starting with standard Fe-alloys have magnetic properties similar to those of bulk metallic glass produced with high-purity elements.

Table 3. Coercivity measurements on $Fe_{36}CO_{36}Nb_4B_{19.2}Si_{4.8}$

	Base materials	State	Coercivity (A/m)
Present invention 1	Industrial Fe-alloys	Amorphous	8
Present invention 2	Industrial Fe-alloys	Amorphous	5
Comparative example 1	Industrial Fe-alloys	Partially amorphous	7000
Comparative example 2	Pure elements	Amorphous	4.5

Claims

1. An amorphous metallic product, formed of an alloy having a chemical formula of

$$Fe_{100-a-b-c-d-x-y}\ M_aNb_bSi_cB_dI_xJ_y$$

wherein :

- M is Co and/or Ni,
- I is one or more elements of the group consisting of Al, Cr, Cu, Mn, C and P,
- J is one or more elements of the group consisting of Ti, S, N and O
- and wherein a, b, c, d, x and y are satisfying the following conditions : 0wt.%≤a≤46.1wt.%, 5.4wt.%≤b≤12.4wt.%, 2.2wt.%≤c≤4.4wt.%, 2wt.%≤d≤6wt.%, x≤2wt.% and y≤0.2wt.%.

2. The product according to claim 1, wherein 0.05≤x≤2wt.% and 0.01≤y≤0.2wt.%.

3. The product according to claim 1, wherein x≤lwt.% and/or y≤0.1wt.%.

4. The product of any one of claims 1 to 3, wherein the O-level is lower than or equal to 0.05wt%.

5. The product according to any one of claims 1 to 4, wherein said product is a bulk metallic product.

6. The product according to claim 5, wherein said product is a ring core for a differential switchgear, said ring core having a thickness higher than 300μm.

7. The product according to claim 5 or 6, wherein said product has magnetic properties defined by

- coercivity between 0.5A/m and 10A/m, and
- relative magnetic permeability between 50000 and 500000

8. A process for producing an amorphous Fe-based product according to any one of claims 1 to 7, the process comprising the steps of :

- Providing starting materials, comprising Fe-containing alloys,
- Melting said starting materials to a temperature above the melting temperature of said materials,
- Keeping the materials in a molten state,
- Pouring the molten materials into a mould,
- Cooling the molten material, to obtain the product.

9. The process according to claim 8, wherein said starting materials comprise one or more of the following : electrolytic Fe, AK-steel, FeB, FeSi, FeNb.

10. The process according to claim 9, wherein the starting materials further comprise pure Co.

11. The process according to claim 9 or 10, wherein said starting materials are defined by the following compositions (in wt%) :

	Electrolytic-Fe	Ak-steel	FeB	FeSi	FeNb	Pure Co
C	0.0005-0.1	0.0005-0.1	0.01-0.5	0.001-0.3	0.001-0.3	-
Mn	0.0001-0.2	0.001-0.5	0.01-2	0.01-1	0.01-1	-
Si	0.0001-0.1	0.0001-0.3	0.01-2	62-75	0.2-3	-
P	0.0005-0.03	0.0005-0.1	0.0005-0.1	0.0005-0.1	0.0005-0.1	-
S	0.0001-0.05	0.0005-0.01	0.0005-0.1	0.0005-0.1	0.0005-0.2	-
Al	0.0001-0.2	0.0001-0.4	0.001-0.8	0.001-0.8	0.001-1.2	-
Ti	0.0001-0.1	0.0001-0.1	0.0001-1	0.0001-1	0.0001-1	-
Nb	0.0001-0.1	0.0001-0.1	0.0001-0.1	0.0001-0.1	60-74	-
Cu	0.0001-0.08	0.001-0.1	0.001-0.3	0.001-0.1	0.001-0.3	-
Cr	0.0001-0.08	0.001-0.1	0.001-0.5	0.001-0.1	0.001-0.1	-
Ni	0.0001-0.08	0.001-0.1	0.001-0.3	0.001-0.1	0.001-0.1	-
As	0.0001-0.02	0.0001-0.05	0.0001-0.1	0.0001-0.05	0.0001-0.05	-
Sn	0.0001-0.02	0.0001-0.05	0.0001-0.1	0.0001-0.05	0.0001-0.05	-
O	0.001-0.1	0.0005-0.1	0.002-0.1	0.001-0.05	0.001-0.05	-
N	0.0003-0.01	0.0005-0.02	0.0005-0.05	0.0005-0.02	0.0005-0.02	-
B	0.0001-0.001	0.0001-0.001	15-21	0.0001-0.001	0.0001-0.001	-
Mo	0.0001-0.05	0.001-0.1	0.001-0.3	0.001-0.1	0.001-0.1	-

(continued)

	Electrolytic-Fe	Ak-steel	FeB	FeSi	FeNb	Pure Co
Zr	0.001-0.05	0.001-0.08	0.001-0.2	0.001-0.1 1	0.001-0.1	-
V	0.0001-0.1	0.0001-0.1	0.0001-0.5	0.0001-0.3	0.0001-0.3	-
Co	0.0001-0.1	0.0001-0.1	0.0001-0.1	0.0001-0.1	0.0001-0.1	99.5-99.95
Fe	Rest	Rest	78.3	22.9	28.9	-

12. The process according to any one of claims 8 to 11, wherein said melting step is performed in a levitation melter.

13. The process of any one of claims 8 to 12, wherein said process is used to produce a master alloy, and wherein said process is followed by the steps of :

- Introducing the master alloy in a melting device,
- Heating up the master alloy to a temperature above its melting temperature
- Pouring the molten material into a mould
- Cooling the molten material, to obtain the product.

14. The process according to any one of claims 8 to 13, wherein the process includes a step of creating a vacuum in the melting chamber before introducing the starting materials in said chamber, and wherein said melting takes place under a protective atmosphere.

15. The process according to claim 14, wherein said vacuum is defined by a pressure of at least 10^{-1} bar.

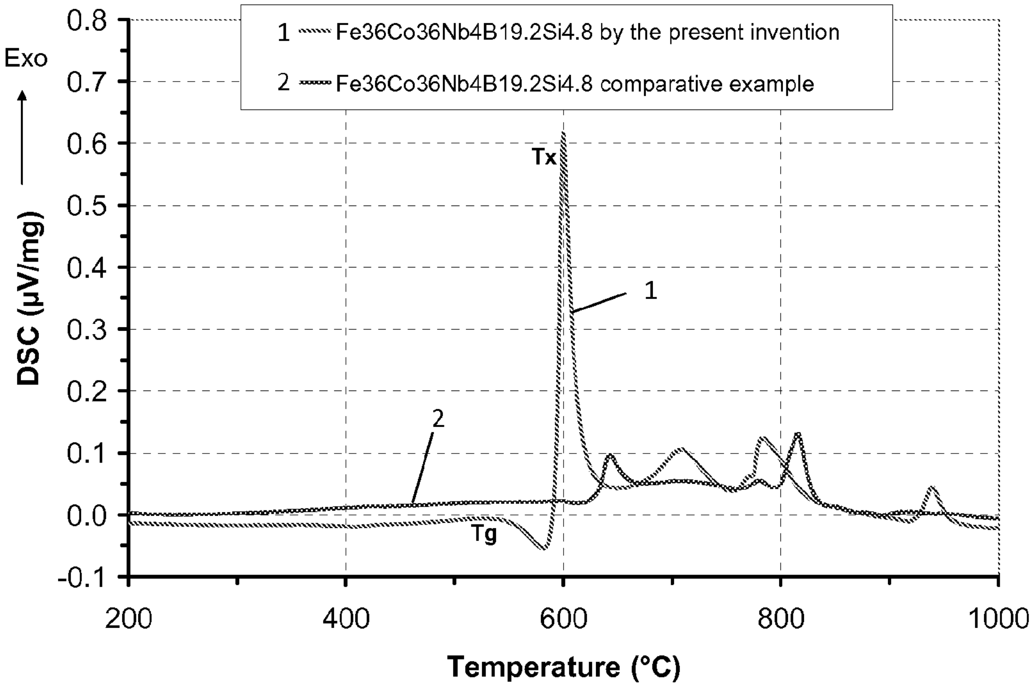
1 Fe36Co36Nb4B19.2Si4.8 by the present invention
2 Fe36Co36Nb4B19.2Si4.8 comparative example
Exo
DSC (µV/mg)
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
-0.1
Tx
Tg
1
2
200
400
600
800
1000
Temperature (°C)

Fig. 1

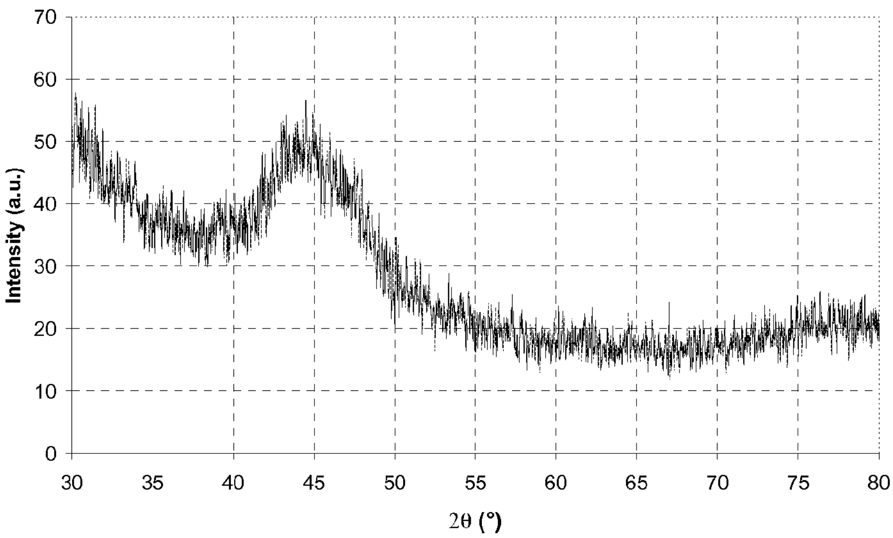
Intensity (a.u.)
70
60
50
40
30
20
10
0
30
35
40
45
50
55
60
65
70
75
80
2θ (°)

Fig. 2

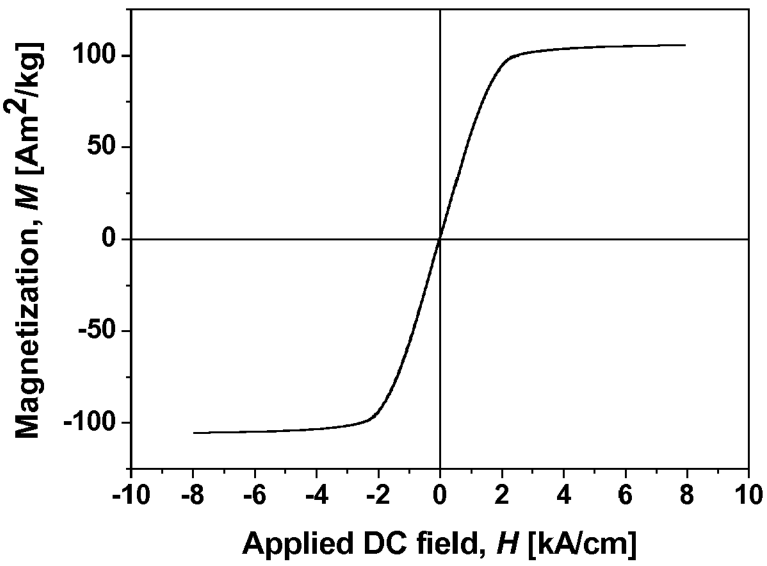
Magnetization, M [Am2/kg]
100
50
0
-50
-100
-10
-8
-6
-4
-2
0
2
4
6
8
10
Applied DC field, H [kA/cm]

Fig. 3

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 08 15 5922

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 A	R.BARRUE ET AL: "Influence of substitution elements on magnetic and thermal properties of amorphous Fe79 B16 Si5 ribbons" PHYSICA SCRIPTA, vol. 37, 1988, pages 356-358, XP009107822 * page 356, left-hand column, paragraph 2 - right-hand column; table 1 *	1,3 8,11-13	INV. C22C1/00 C22C33/00 C22C33/04 C22C33/06 C22C45/00 C22C45/02 C22C45/04
X	US 5 160 379 A (YOSHIZAWA YOSHIHITO [JP] ET AL) 3 November 1992 (1992-11-03) * abstract; claim 1; example 13; table 1 *	1,2	
X	US 2001/054330 A1 (BIZEN YOSHIO [JP] ET AL) 27 December 2001 (2001-12-27) * paragraphs [0022], [0023]; examples 18-20; table 4 *	1	
X	US 2003/041931 A1 (SUNAKAWA JUN [JP] ET AL) 6 March 2003 (2003-03-06) * paragraph [0099]; example 6; table 8 *	1,3	TECHNICAL FIELDS SEARCHED (IPC)
A	EP 0 529 634 A (KAWASAKI STEEL CO [JP]) 3 March 1993 (1993-03-03) * claim 3 *	14,15	C22C H05B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	31 October 2008	Lilimpakis, Emmanuel

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

2

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 08 15 5922

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.

31-10-2008

Patent document cited in search report		Publication date	Patent family member(s)			Publication date
US 5160379	A	03-11-1992	CA	1323219	C	19-10-1993
			DE	3779070	D1	17-06-1992
			EP	0271657	A2	22-06-1988
			JP	2040464	C	28-03-1996
			JP	3219009	A	26-09-1991
			JP	7074419	B	09-08-1995
			US	4881989	A	21-11-1989
US 2001054330	A1	27-12-2001	JP	3722411	B2	30-11-2005
			JP	2001316716	A	16-11-2001
US 2003041931	A1	06-03-2003	NONE			
EP 0529634	A	03-03-1993	JP	5059483	A	09-03-1993
			US	5322113	A	21-06-1994

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