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(54) Method of manufacturing an isotropic permanently magnetic material, isotropic permanently magnetic material and synthetic resin-bound isotropic permanent magnet.

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PATENT ABSTRACTS OF JAPAN vol. 13, no. 2 (E-700)(3350) 06 January 1989, & JP-A-63 213315 (TDK CORP) 06 September 1988,

(73) Proprietor : **N.V. Philips' Gloeilampenfabrieken**
Groenewoudseweg 1
NL-5621 BA Eindhoven (NL)

(72) Inventor : **De Mooij, Dirk Bastiaan**
c/o INT. OCTROOIBUREAU B.V.
Prof. Holstlaan 6
NL-5656 AA Eindhoven (NL)
Inventor : **Keetels, Henricus Arnoldus Antonius**
c/o INT. OCTROOIBUREAU B.V.
Prof. Holstlaan 6
NL-5656 AA Eindhoven (NL)
Inventor : **Eisses, John**
c/o INT. OCTROOIBUREAU B.V.
Prof. Holstlaan 6
NL-5656 AA Eindhoven (NL)
Inventor : **Buschow, Kurt Heinz Jürgen**
c/o INT. OCTROOIBUREAU B.V.
Prof. Holstlaan 6
NL-5656 AA Eindhoven (NL)

(74) Representative : **Weening, Cornelis et al**
INTERNATIONAAL OCTROOIBUREAU B.V.,
Prof. Holstlaan 6
NL-5656 AA Eindhoven (NL)

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Description

The invention relates to a method of manufacturing an isotropic, permanently magnetic material which comprises Nd and/or Pr, Fe and C, the constituents of the material being melted together to form an alloy which is subsequently subjected to a thermal treatment, so that phase transformation takes place. The invention also relates to an isotropic, permanently magnetic material and to a synthetic resin-bound isotropic permanent magnet.

A method of the type mentioned in the opening paragraph is known *per se*. For example, in European Patent Application with publication number 320.064, a description is given of a method in which an alloy of $Nd_2Fe_{14}C$ is subjected to a thermal treatment at 870°C for 500 hours to bring about a phase transformation. In this thermal treatment, the tetragonal "2-14-1" crystal structure is formed which is characteristic of the hard magnetic phase of the known $Nd_2Fe_{14}B$ compound. In the case of $Nd_2Fe_{14}C$, the thermal treatment must take place in a relatively small temperature range of 840°C to 890°C. Above 890°C, said tetragonal crystal structure is not formed. If the thermal treatment takes place at a temperature below 840°C, an impermissibly large quantity of Nd_2Fe_{17} is formed in addition to the desired tetragonal phase.

The known method has disadvantages. It has been found that the magnetic material manufactured by said method has hardly any or no coercive force (H_c) after the phase transformation. The value of the coercive force is smaller than 50 kA/m. Due to said small coercive force the known material is not very suitable for use in synthetic resin-bound isotropic permanent magnets.

One of the objects of the invention is to improve the known method. The invention is more particularly aimed at providing a method of manufacturing an isotropic, permanently magnetic material of the type mentioned in the opening paragraph, which material has coercive force. According to a further object, the invention provides an isotropic, permanently magnetic material having a substantially single-phase crystal structure and a coercive force of at least 150 kA/m. The magnetic material should further have a high saturation magnetization. A further object of the invention is to provide a synthetic resin-bound isotropic permanent magnet.

These and other objects are achieved by a method of the type mentioned in the opening paragraph, which is characterized according to the invention in that the alloy comprises 10-20 at.% of Nd and/or Pr, 70-85 at.% of Fe, 4-11 at.% of C and 0.1-2 at.% of B, and in that the thermal treatment takes place at a temperature between 900°C and 1050°C.

The invention is based on, inter alia, the experimentally gained insight that the temperature range in which phase transformation takes place can be considerably extended by substituting a small quantity of C of the known $Nd_2Fe_{14}C$ by B. In the known $Nd_2Fe_{14}C$, phase transformation only takes place in the range from 840°C to 890°C, yet in the case of the material according to the invention the formation of the tetragonal phase takes place in the temperature range from 800 to 1050°C. Surprisingly, it has further been found that when the thermal treatment is carried out at 900-1050°C, the material exhibits a coercive force of at least 150 kA/m. When the thermal treatment takes place at temperatures between 800°C and 900°C, an isotropic permanently magnetic material is obtained having a coercive force which is smaller than 150 kA/m. When the thermal treatment is carried out at temperatures above 1050°C hardly any or no tetragonal phase is obtained.

The rare earth metal content in the alloy should consist exclusively or almost exclusively of Nd and/or Pr. This provides the magnetic material according to the inventive method with a high saturation magnetization. A small quantity of other rare earth metals (up to 10 at.%) may be suitable to influence certain magnetic properties of the material. Preferably, however, the material comprises only Nd as the rare earth metal. In this manner, the highest saturation magnetization is attained.

The isotropic, permanently magnetic material obtained according to the inventive method comprises exclusively or substantially exclusively Fe as the transition metal. Under certain conditions it might be advantageous for the material to also comprise a small quantity of Co as the transition metal (up to 10 at.%). Co increases the Curie temperature and the corrosion resistance of the magnetic material. Co-containing magnets can moreover be oriented at much smaller fields than magnets containing only Fe as the transition metal. In the case of the latter magnets, fields of at least 5 T are required. Co-containing magnets can already be optimally oriented at 2.0 T. If, however, a maximum saturation magnetization is aimed at, only Fe is to be used as the transition metal.

As mentioned above, the presence of a relatively small quantity of B in the magnetic material is essential for the inventive method. B takes up the lattice site of C in the crystallized "$Nd_2Fe_{14}C$"-structure. The molar quantity of B is at least 2.5 % of the overall content of B and C. At a smaller content of B, the tetragonal phase is insufficiently formed by recrystallization in the temperature range of 900-1050°C. The molar quantity of B is maximally 15 % of the overall content of B and C. At a larger quantity of B, recrystallization results in multiphase material being formed. This is regarded as a disadvantage.

It is noted that a large number of $R_2Fe_{14}CxB_{1-x}$-compounds are known from Fig. 1 of J. Appl. Phys. 61 3574

(1987). R denotes a rare earth metal. In said Figure, a range is indicated in which the $Fe_{77}R_{15}(B, C)_8$-compounds form a continuous series. In the Figure several compositions are given which comprise only Nd as the rare earth metal and which, in addition to C comprise a small quantity of B. These compounds, however, have been subjected to a thermal treatment at 800°C and, consequently, have no appreciable coercive force.

Further, it is noted that in Mat. Lett. 4 378 (1986) a description is given of the compound $Fe_{77}Nd_9Dy_6C_{7.2}B_{0.8}$ which has a H_c of 12.5 kOe. It is known *per se* that the rare earth metal Dy provides a considerable coercive force to tetragonal 2-14-1-compounds of the type $R_2Fe_{14}B$.

An interesting embodiment of the method according to the invention is characterized in that the alloy is subjected to the thermal treatment for maximally 4 days. In the case of the method known from EP 320.064, a heat treatment of at least approximately one week is necessary to bring about the desired tetragonal crystal structure in the alloy. With a view to an economical production, such long thermal treatments are undesirable.

A further advantageous embodiment of the method according to the invention is characterized in that the alloy is ground to form a magnetic powder having an average particle size of 2 to 40 μm. It has been found that the coercive force of the magnetic material increases considerably when, following the thermal treatment, the alloy is ground to form a magnetic powder having an average particle size of 2-40 μm. The grinding operation is carried out in, for example, a ball mill. After grinding, magnetic powders are obtained having a H_c of at least 500 kA/m.

The invention further relates to an isotropic permanently magnetic material. According to the invention, said material is characterized in that it comprises 10-20 at.% of Nd and/or Pr, 70-85 at.% of Fe, 4-11 at.% of C and 0.1-2 at.% of B, and in that the material has a coercive force of at least 150 kA/m. Said material is preferably powderous and has an average particle size of 2-40 μm and a coercive force of at least 500 kA/m. Such a powder can be advantageously used in a synthetic resin-bound, isotropic, permanent magnet.

The invention further relates to a synthetic resin-bound, isotropic, permanent magnet. According to the invention, said magnet is characterized in that it comprises an isotropic, permanently magnetic material which is composed of 10-20 at.% of Nd and/or Pr, 70-85 at.% of Fe, 4-11 at.% of C and 0.1-2 at.% B, and which is powderous with an average particle size in the range between 2 and 40 μm, and in that the material has a coercive force of at least 500 kA/m.

The invention will be explained in greater detail by means of exemplary embodiments and with reference to the accompanying drawing, in which

Fig. 1 shows the maximum temperature T(°C) at which the isotropic, magnetic material $Nd_2Fe_{14}C_{1-x}B_x$ or $Pr_2Fe_{14}C_{1-x}B_x$ can be formed as a function of the B-content x.

Fig. 2 shows the effect of the grinding time t(min.) on the coercive force H_c (kA/m) of an alloy of composition $Nd_{15}Fe_{77}C_{7.68}B_{0.32}$.

Fig. 3 shows a hysteresis loop of a magnetic alloy of the composition $Nd_{16}Fe_{75}C_{8.55}B_{0.45}$.

A number of alloys comprising 10-20 at.% of Nd and/or Pr, 70-85 at.% of Fe, 4-11 at.% of C and 0.1-2 at.% of B was manufactured. For this purpose, a mixture of the constituents in the desired ratio was melted together by means of an arc at approximately 1800°C. The alloys were subsequently sealed into glass capsules under a vacuum and then subjected to a thermal treatment to bring about phase transformation. The duration and the temperature of the thermal treatment were varied. X-ray analysis showed that the crystallized alloys were substantially completely single-phase and exhibited a tetragonal structure. The coercive force of the unground alloys was determined.

The alloys were subsequently ground in a ball mill, under an inert atmosphere (nitrogen or vacuum), to form a powder having an average particle size ranging between 2 and 40 μm. For several alloys the variation of the H_c as a function of the grinding duration was investigated. For this purpose, the ground powders were fixed in a synthetic resin. During the fixing operation, the powder particles were oriented by means of a magnetic field. The alloys 1-9 were oriented using a field of 5 T. The alloys 10-12 were oriented using a field of 2.0 T. The H_c of these magnets was measured by means of a vibrating sample magnetometer.

Table

1	2	3	4	5	6	7
1.	$Nd_{15}Fe_{77}C_{7.36}B_{0.64}$	4	900	194	650	77
2.	$Nd_{15}Fe_{77}C_{7.68}B_{0.32}$	4	900	232	663	75
3.	$Nd_{15}Fe_{77}C_{7.84}B_{0.16}$	4	900	178	567	78
4.	$Nd_{16}Fe_{73.5}C_{10}B_{0.5}$	8	900	253	657	65
5.	$Nd_{16}Fe_{73.5}C_{9}B_{1.5}$	2	1050	278	617	-
6.	$Nd_{20}Fe_{73.5}C_{6.1}B_{0.4}$	8	900	344	600	67
7.	$Nd_{2}Fe_{14}C_{0.97}B_{0.03}$	14	950	389	539	93
8.	$Nd_{15.6}Fe_{74.4}C_{9.5}B_{0.5}$	3	900	344	614	64
9.	$Nd_{16}Fe_{75}C_{8.55}B_{0.45}$	5.5	900	389	575	87
10.	$Nd_{16}Fe_{70}Co_{4}C_{9.5}B_{0.5}$	3	950	650	-	-
11.	$Nd_{16}Fe_{70}Co_{4}C_{9.5}B_{0.5}$	3	980	680	-	-
12.	$Nd_{16}Fe_{70}Co_{4}C_{9.5}B_{0.5}$	3	1000	630	-	-

The Table shows a number of compositions and properties of the alloys which were manufactured by the method according to the invention. Column 1 lists the number of the exemplary embodiment. Column 2 lists the composition of the alloys. The duration (days) and the temperature (°C) of the thermal treatment are listed in column 3 and column 4, respectively. The coercive force (kA/m) of the recrystallized alloy before and after the grinding operation are listed in column 5 and column 6, respectively. The grinding operation took place in a ball mill for 10-20 minutes, until an average grain size was attained which ranges between 2 and 40 μm. Column 7 lists the saturation magnetization (emu/g) of the synthetic resin-bound isotropic permanent magnets obtained by fixing the powder in wax. The energy product $B.H_{max}$ of the magnets based on alloys 10-12 was approximately 70 kJ/m³.

A number of alloys having the general composition $Nd_{16}Fe_{75}(C_{1-x}B_x)_9$ were subjected to closer investigation. As described above, the alloys were manufactured by arc melting. Subsequently, they were subjected to a heat treatment at 900°C for 5.5 days. The measured coercive force (H_c) values of these alloys were 290 kA/m (x=0.01); 430 kA/m (x=0.03); 500 kA/m (x=0.05) and 440 kA/m (x=0.1). At values of x=0 and x=0.25, the H_c of the alloys was smaller than 150 kA/m.

Further, a number of alloys having the general formula $Nd_{16}Fe_{74-x}Co_xC_{9.5}B_{0.5}$ were manufactured by arc melting. In said alloys the value of x was varied between 0 and 10. It was found that after annealing and orienting the Co-containing alloys, the coercive force of said alloys was much higher than that of similar alloys which do not contain Co. Besides, the Co-containing magnets could be optimally oriented with a magnetic field of 2.0 T. Similar magnets which do not contain Co require fields of at least 5.0 T. Moreover, the duration of the necessary annealing treatment was shorter. Thus, it was found that after annealing for 6 hours at 950°C $Nd_{16}Fe_{70}Co_4C_{9.5}B_{0.5}$ already has a coercive force of 600 kA/m. Similar magnets without Co require a grinding step to attain said value (see Table). After an annealing treatment at 950°C for 15 minutes, it appeared that the alloy $Nd_{16}Fe_{72}Co_2C_{9.5}B_{0.5}$ already had a coercive force of 510 kA/m.

Fig. 1 shows the effect of a small substitution of C by B in $Nd_2Fe_{14}C$ on the maximum transformation temperature. Above the line shown, the intended tetragonal phase is not achieved. When approximately 2.5% of B is added, related to the overall content of C and B, it is found that the maximum transformation temperature has risen from 890°C to 1050°C.

Fig. 2 shows the effect of grinding (duration t in min.) on the coercive force (H_c, kA/m) of an alloy obtained according to the inventive method (exemplary embodiment 2). The grinding operation almost tripled the coercive force. The Figure further shows that too long a grinding treatment adversely affects the coercive force of

the powder.

Fig. 3 shows the hysteresis loop of a magnetic alloy having the composition $Nd_{16}Fe_{75}C_{8.55}B_{0.45}$ at a magnetic field of 5 T. The alloy was heated at 950°C for 1 day. The remanence was 0.65 T.

Claims

1. A method of manufacturing an isotropic permanently magnetic material which comprises Nd and/or Pr, Fe and C, the constituents of the material being melted together to form an alloy which is subsequently subjected to a thermal treatment, so that phase transformation takes place, characterized in that the alloy comprises 10-20 at.% of Nd and/or Pr, 70-85 at.% of Fe, 4-11 at.% of C and 0.1-2 at.% of B, and in that the thermal treatment takes place at a temperature between 900°C and 1050°C.

2. A method as claimed in Claim 1, characterized in that the alloy is subjected to the thermal treatment for maximally 4 days.

3. A method as claimed in Claim 1 or 2, characterized in that the alloy is ground to form a magnetic powder having an average particle size of 2 to 40 μm.

4. Isotropic permanently magnetic material, characterized in that the material comprises 10-20 at.% of Nd and/or Pr, 70-85 at.% of Fe, 4-11 at.% of C and 0.1-2 at.% of B, and in that the material has a coercive force of at least 150 kA/m.

5. Isotropic permanently magnetic material as claimed in Claim 4, characterized in that the material also contains Co in a quantity of maximally 10 at%.

6. A synthetic resin-bound, isotropic, permanent magnet, characterized in that the magnet comprises an isotropic, permanently magnetic material as claimed in Claim 4 or 5.

Patentansprüche

1. Verfahren zum Herstellen eines isotropen, dauermagnetischen Werkstoffs, der Nd und/oder Pr, Fe und C enthält, wobei die bestandteile des Werkstoffs zu einer Legierung zerschmolzen werden, die danach einer Wärmebehandlung ausgesetzt wird, so daß Phasentransformation auftritt, dadurch gekennzeichnet, daß die Legierung 10-20 at. % Nd und/oder Pr, 70-85 at. % Fe, 4-11 at. % C und 0,1-2 at. % B aufweist, und daß die thermische behandlung bei einer Temperatur zwischen 900°C und 1050°C erfolgt.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Legierung maximal 4 Tage lang der thermischen Behandlung ausgesetzt wird.

3. Verfahren nach Anspruch 1 oder 2, dadurch gekennzeichnet, daß die Legierung zu einem Magnetpulver mit einer mittleren Teilchengröße von 2 bis 40 μm zermahlen wird.

4. Isotroper dauermagnetischer Werkstoff, dadurch gekennzeichnet, daß er 10-20 at. % Nd und/oder Pr, 70-85 at. % Fe, 4-11 at. % C und 0,1-2 at. % B aufweist, und daß der Werkstoff eine Koerzitivkraft von mindestens 150 kA/m hat.

5. Isotroper dauermagnetischer Werkstoff nach Anspruch 4, dadurch gekennzeichnet, daß er ebenfalls Co in einer Menge von maximal 10 at. % enthält.

6. Kunststoffgebundener isotroper Dauermagnet, dadurch gekennzeichnet, daß er einen isotropen, dauermagnetischen Werkstoff nach Anspruch 4 oder 5 enthält.

Revendications

1. Procédé pour la fabrication d'un matériau isotrope à aimantation permanente comportant du Nd et/ou du Pr, du Fe et du C, les constituants du matériau étant fondus conjointement de manière à constituer un

alliage qui est ensuite soumis à un traitement thermique, de sorte qu'il se produit une transformation de phase, caractérisé en ce que l'alliage comporte du Nd et/ou du Pr dont la teneur en atomes est comprise entre 10 et 20%, du Fe dont la teneur en atomes est comprise entre 70 et 85 %, du C dont la teneur en atomes est comprise entre 4 et 11 % en atomes et du B dont la teneur en atomes est comprise entre 0,1 et 2%, et en ce que le traitement thermique se déroule à une température comprise entre 900 et 1050°C.

2. Procédé selon la revendication 1, caractérisé en ce que l'alliage est soumis au traitement thermique pendant quatre jours tout au plus.

3. Procédé selon la revendication 1 ou 2, caractérisé en ce que l'alliage est broyé de manière à constituer une poudre magnétique dont la grosseur de particule moyenne est comprise entre 2 et 40 μm.

4. Matériau isotrope à aimantation permanente, caractérisé en ce que sa teneur en Nd et/ou en Pr est comprise entre 10 et 20% en atomes, sa teneur en Fe est comprise entre 70 et 85% en atomes, sa teneur en C est comprise entre 4 et 11% en atomes et sa teneur en B est comprise entre 0,1 et 2% en atomes, et en ce que le matériau présente une force coercitive qui est au moins égale à 150 kA/m.

5. Matériau isotrope à aimantation permanente selon la revendication 4, caractérisé en ce que le matériau contient également du Co dans une quantité qui est tout au plus égale à 10 % en atomes.

6. Aimant permanent isotrope lié par résine synthétique caractérisé en ce que l'aimant comporte un matériau isotrope à aimantation permanente selon la revendication 4 ou 5.

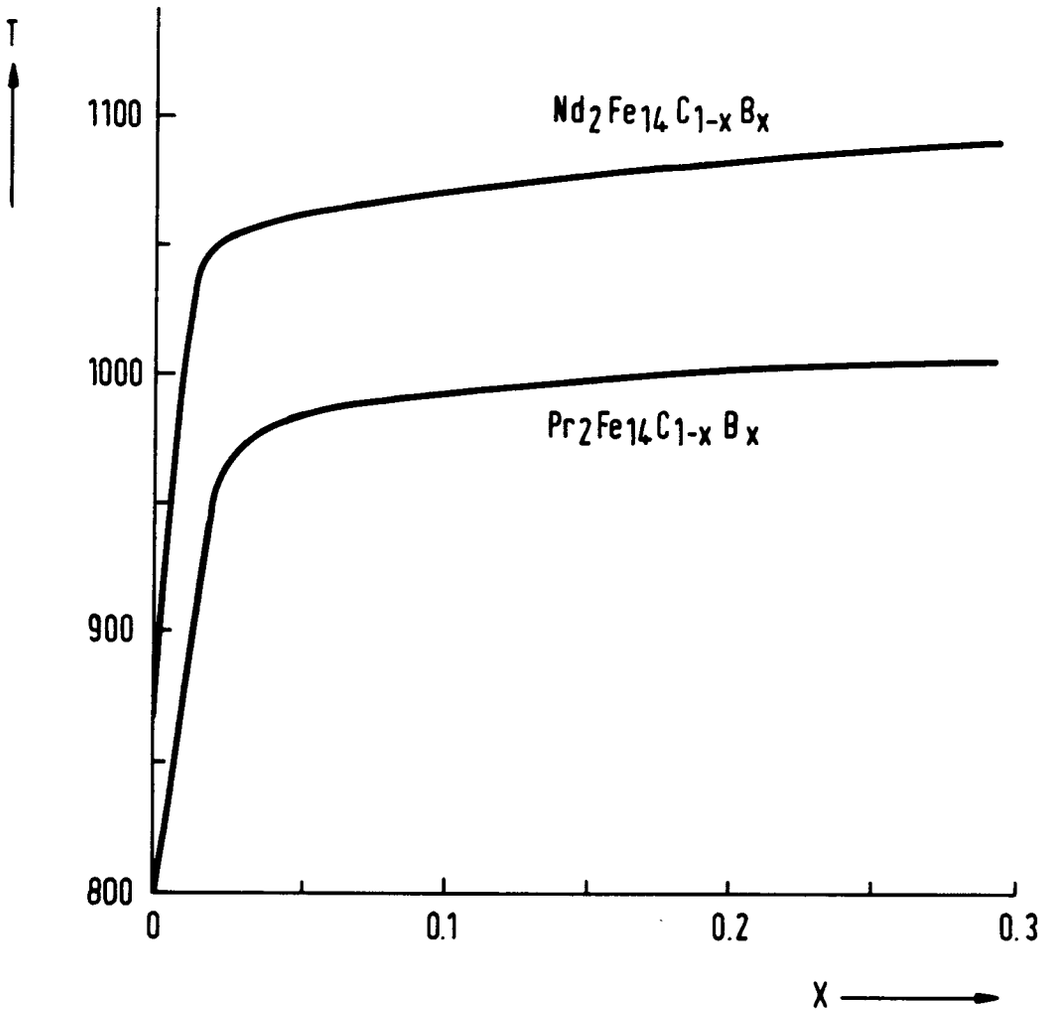
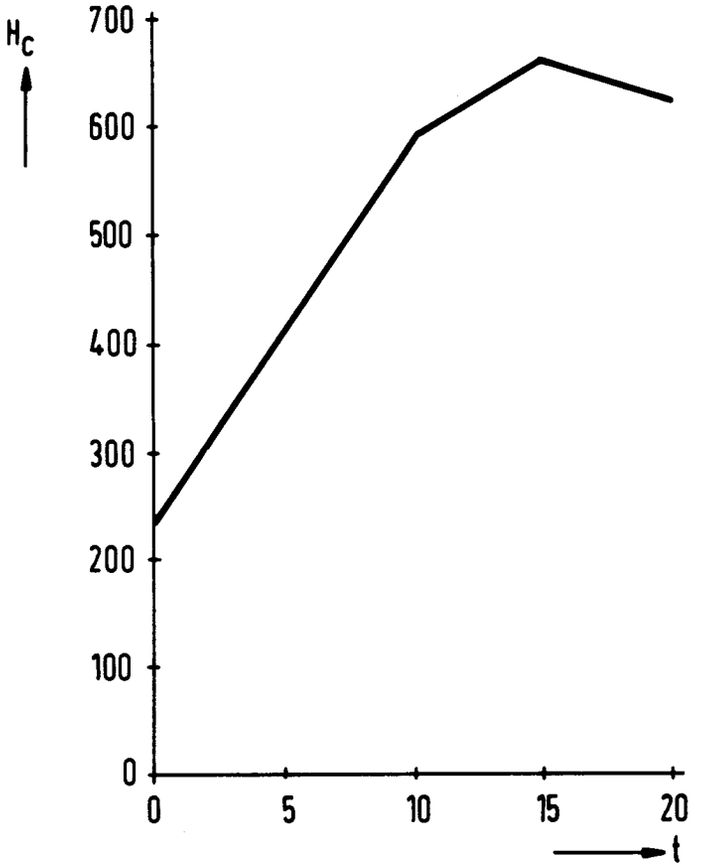


FIG.1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400
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200
100
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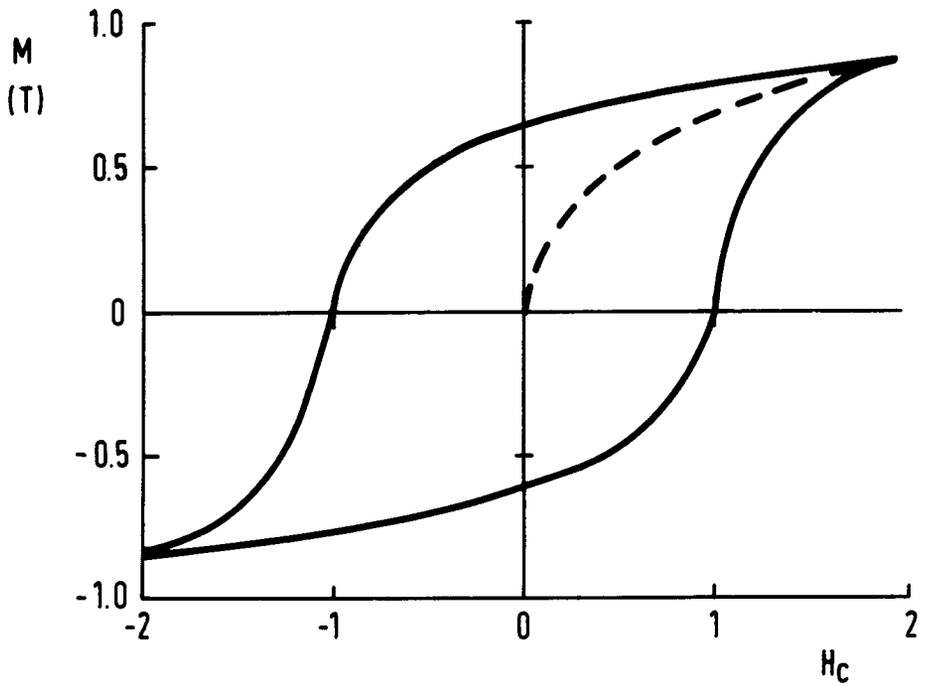
0
5
10
15
20
t

FIG.2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(T)
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-1
0
1
2
Hc

FIG.3