

1

2,900,344

MAKING ANISOTROPIC PERMANENT MAGNETS

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This invention relates to magnetically-anisotropic permanent magnets and to a method of making the same.

The copending United States patent application Serial No. 239,264, filed July 30, 1951, of Went et al., now Patent 2,762,777, describes a permanent magnet material formed essentially of hexagonal crystals of the composition $MO.6Fe_2O_3$ in which M designates one of the metals barium, strontium and lead, one of the later metals being replaceable by calcium for an atom fraction of 0.4. While such magnetic materials are inexpensive and have excellent magnetic properties, for instance high coercive force and remanence, the BH_{max} value is rather low, i.e., about 1.1×10^6 Gauss-Oersted, compared to that of some other types of permanent magnetic materials.

As described in the copending United States patent application Serial No. 325,202, filed December 10, 1952, of Gorter et al., now Patent 2,762,778, it has been proposed to increase the BH_{max} value of the above-mentioned types of magnetic materials by forming the material in a powder form into magnetically-anisotropic permanent magnets and this may be effected in various ways. For example, fine particles of the material, for instance having a grain size less than about 10μ , are placed in a mobile condition, i.e., one in which the particles are sufficiently movable so that they can be magnetically oriented when subjected to the action of a magnetic field having a field strength of more than about 100 Oersted, preferably greater than 700 Oersted. The particles after being oriented by a magnetic field are then compressed, preferably while maintaining the magnetic field, into a compacted body which is then sintered at a temperature of about $900^\circ C.$ to $1450^\circ C.$ Although the temperature required for sintering is above the Curie point and the heating may give rise to some crystal growth, the orientation of the particles is maintained, and may even be improved during the sintering operation. Such magnetically-anisotropic permanent magnets have a BH_{max} value more than 1.1×10^6 Gauss-Oersted and up to about 1.75×10^6 Gauss-Oersted.

The main object of the present invention is to produce permanent magnets of the above type of materials which have a higher BH_{max} value while retaining the other advantageous magnetic properties of magnets made of such materials.

A more specific object is to provide permanent magnets of such materials which have a BH_{max} of more than 2.3×10^6 Gauss-Oersted and preferably more than 2.9×10^6 Gauss-Oersted.

A further object is to provide a new and novel method of making such magnetically-anisotropic permanent magnets.

The permanent magnets according to the invention have a BH_{max} value greater than 2.3×10^6 Gauss-Oersteds, preferably greater than 2.9×10^6 Gauss-Oersteds and consist of a magnetically-anisotropic body comprising, as the constituents essential for the permanent magnetic properties, crystals having a magneto-plumbite structure. These crystals consist of at least one compound having

2

the formula $MO.6Fe_2O_3$ in which M designates at least one of the metals Ba, Sr, and Pb; an atom fraction of not more than 0.4 of at least one of said metals being replaceable in the crystal by calcium.

Although the above-mentioned patent applications state that the permanent magnetic crystals in the sintered product must have approximately the size of the Weiss domains of the substances concerned, we have found that other factors influence the $(BH)_{max}$ value and that by controlling these factors an unexpectedly large increase in this value can be obtained. More particularly we have found that the size and distribution of the crystallites constituting the magnetic body influence the $(BH)_{max}$ value and that if the size and distribution is such that the spaces or voids between the larger crystallites is filled with crystallites of smaller size, unexpectedly large values of $(BH)_{max}$ are realized. Moreover, the relative quantities of the different size crystallites should be such that the quantity of smaller crystallites will not exceed that amount which will fill the spaces between the larger crystallites in order that a high "filling factor" is obtained.

In the manufacture of such magnetically anisotropic bodies, the large and small crystallites are compressed into a body and sintered to unite the crystallites into a body. The sintering and cooling of the body must be carefully controlled to avoid excessive recrystallization and undue crystal growth which would detrimentally affect the coercive force. Preferably, a recrystallization inhibitor is included in the mass of crystallites to be compacted by pressing and sintering. Such recrystallization inhibitors or "modifiers" as they will hereinafter be referred to may be formed during the preparation of the magnetic material prior to preparing an anisotropic magnetic body therefrom. More particularly, certain substances which are contained in the starting material and have not reacted to form $MO.6Fe_2O_3$, or which have undergone a different chemical conversion, may act as sintering agents. These sintering agents are first at least partly dissolved in the permanent magnetic crystal phase and then separate out as a second phase during the cooling which is effected after the sintering. The second phase separated out hinders the magnetization as far as it is due to a shift in the Bloch's walls.

Substances of the above type, which will be referred to hereinafter as "modifiers" may be, for example, barium ferrite or calcium ferrite which are produced during the manufacture of the permanent magnetic material from barium carbonate or calcium carbonate respectively, when these latter compounds are present in the starting material in an excess quantity compared with the quantity of iron oxide in the ratio M:F of 1:12.

Instead of forming the modifiers in the permanent magnetic material they may be added afterwards, i.e., just before the particles of permanent magnetic material are formed into magnetically-anisotropic bodies. For this purpose we may mix with the permanent magnetic materials, a barium compound such as barium carbonate, barium sulphate, barium oxide and barium ferrite, or a calcium compound such as calcium carbonate, calcium oxide and calcium ferrite.

In another embodiment we add to the starting material or to the permanent magnetic material prior to the formation of the magnetically-anisotropic body, modifiers which neither form compounds of the type MO as defined above nor produce this compound by heating. As such modifiers we may use compounds of lanthanum, bismuth, arsenic, antimony and boron such as lanthanum oxide, bismuth oxide, boric oxide, arsenic trioxide, antimony pentoxide or compounds which produce one of these substances when heated. To produce the best improvement in the BH_{max} values, the modifiers should be present in

3

amounts of about 0.01 to 1% by weight of the quantity of the $\text{MO.6Fe}_2\text{O}_3$ crystals.

The invention will be described in connection with the following examples which are illustrative only, the scope of the invention being defined in the claims forming a part of this specification.

Example I

430 gr. of barium carbonate (99.83% by weight of pure BaCO_3) and 1920 gr. of iron oxide (99.78% by weight of pure Fe_2O_3) were ground, after 2 litres of alcohol were added, in a ball mill for two hours. The alcohol was evaporated and the powder sintered in a passage furnace at a rate of passage of 20 mms. per minute. In this furnace the mixture was heated at an average rate of 46°C . per minute to a temperature of 1250°C . and kept at this temperature for 5 minutes followed by cooling at the same rate. The powder was then ground in the manner referred to above for 16 hours, freed from alcohol and sintered in a passage furnace at the rate of passage of 2.5 mms. per minute. Thus the powder was heated at an average rate of 33°C . per minute to a temperature of about 1340°C ., at which it was kept for about 8 minutes followed by cooling again at a rate the same as the heating rate. The powder was again ground with alcohol in a ball mill for 24 hours, freed from alcohol and a quantity of lanthanum oxide (La_2O_3) of 0.5% by weight of the quantity of powder was added thereto and the substances thoroughly mixed in a mortar. This powder was introduced into a pressing magnet comprising an iron yoke, surrounded by a coil and having an air gap, one of the two poles of which was movable in vertical direction. A brass mold having a steel templet was filled with the compressed material in a ratio by weight of the powder and a liquid such as water, alcohol, or acetone varying between 2:1 and 2:3, and introduced into the air gap in a manner such that the bottom side of the upper pole engaged the upper side of the templet. The coil was energized and the movable pole was pressed down by means of a lever. After the pressing ended, the coil was deenergized. Thus a plurality of pastils were moulded which were then heated to a temperature of about 1200°C . to 1225°C . for 7 minutes. The physical and magnetic properties of the materials thus obtained essential for the permanent magnetic properties are indicated in the following table.

	Sintered at $1,200^\circ\text{C}$.	Sintered at $1,225^\circ\text{C}$.
Density (g./cm. ³)	4.69	4.91
B_r (in Gauss)	3,300	3,490
I^H_c (in Oersted)	1,910	1,460
B^H_c (in Oersted)	1,800	1,400
$(BH)_{\max}$ (in Gauss-Oersted)	2.37×10^6	2.27×10^6

Example II

341 gr. of barium carbonate (99.2% by weight of pure BaCO_3) and 1661 gr. of iron oxide (99.83% by weight of pure Fe_2O_3) were ground in a dry state for 15 minutes. Then 5% by weight of water was added and the grinding operation continued for 10 minutes. The mixture was then compressed to form tablets having a diameter of about 7 cms. and a thickness of about 2 to 4 cms. These tablets were heated to 1270°C . for about 15 minutes in a furnace, the temperature of 1200°C . being reached within 10 hours. The temperature was then raised from 1200°C . to 1270°C . within one hour followed by cooling from 1270°C . to 1200°C . within 30 minutes. From 1200°C . the temperature was reduced to room temperature within 24 hours. After cooling the tablets were reduced by grinding in the dry state for 30 minutes followed by grinding in alcohol in a vibrating mill for 4 hours. The alcohol was evaporated, after which the

4

powder was mixed in a mortar with 0.25% by weight of lanthanum oxide (La_2O_3). The mixture obtained was then magnetically oriented in a pressing magnet in the manner described in Example I. The pastils obtained were then heated in a passage furnace maintained at a temperature of about 1320°C . for about 10 minutes with a rate of passage of about 10 mms. per minute. The sintered pastils had the following properties:

Density (in g./cm. ³)	4.58
B_r (in Gauss)	3400
I^H_c (in Oersted)	2080
B^H_c (in Oersted)	1950
$(BH)_{\max}$ (in Gauss-Oersted)	2.52×10^6

Example III

A magnetic powder was produced from 341 gr. of barium carbonate (99.2% by weight of pure BaCO_3) and 1661 gr. of iron oxide (99.83% by weight of pure Fe_2O_3) in the manner described in Example II. This powder was then mixed in a mortar with 0.5% by weight of basic bismuth carbonate and the mixture worked to form sintered pastils in the manner described in Example II. The properties of the pastils obtained were as follows:

Density (in g./cm. ³)	4.70
B_r (in Gauss)	3550
I^H_c (in Oersted)	1830
B^H_c (in Oersted)	1680
$(BH)_{\max}$ (in Gauss-Oersted)	2.70×10^6

Example IV

A magnetic powder was produced in the manner referred to under Example II. This powder was mixed in a ball mill with 1% by weight of calcium carbonate and the mixture worked up to form pastils in a pressing magnet in the manner described in Example I. The pastils were then heated in a passage furnace at the rate of passing of about 10 mms. per minute, the heating temperature, which was maintained for about 10 minutes, being 1275°C . The sintered pastils had the following properties:

Density (in g./cm. ³)	4.80
B_r (in Gauss)	3440
I^H_c (in Oersted)	1740
B^H_c (in Oersted)	1630
$(BH)_{\max}$ (in Gauss-Oersted)	2.53×10^6

Example V

A magnetic powder was produced in the manner described in Example II. This powder was worked up to form pastils in the manner described in Example I. The pastils obtained were heated in a passage furnace at a rate of passing of about 10 mms. per minute, the heating temperature, which was maintained for about 10 minutes, being 1300°C . The pastils had the following properties:

Density (in g./cm. ³)	4.37
B_r (in Gauss)	3340
I^H_c (in Oersted)	1700
B^H_c (in Oersted)	1590
$(BH)_{\max}$ (in Gauss-Oersted)	2.35×10^6

From a comparison of the Examples II to V it appears that additions such as lanthanum oxide, basic bismuth carbonate and calcium carbonate favorably affect the $(BH)_{\max}$ value.

Example VI

The magnetic powder was produced in the manner described in Example II, the difference being, however, that grinding was continued in a vibrating mill not for 4 hours but for 16 hours in alcohol. The magnetic powder was worked up to form sintered pastils in the manner

5

described in Example V. The pastils obtained had the following properties:

Density (in g./cm. ³)	4.29
B _r (in Gauss)	3160
I ^H c (in Oersted)	1720
B ^H c (in Oersted)	1590
(BH) _{max} (in Gauss-Oersted)	2.02×10 ⁶

It appears herefrom that excessive prolongation of the grinding operation may adversely affect the permanent magnetic properties.

Example VII

341 gr. of barium carbonate (99.2% by weight of pure BaCO₃) and 1661 gr. of iron oxide (99.83% by weight of pure Fe₂O₃) were ground in the dry state for 15 minutes. Then 5% by weight of water was added and the grinding operation was continued for 10 minutes. The mixture was then compressed to form tablets having a diameter of about 7 cms. and a thickness of about 2-4 cms. These tablets were heated at 1280° C. for about 5 minutes in a furnace at a heating rate of about 170° C. and a cooling rate of about 190° C. per hour. After cooling the tablets were reduced by grinding in the dry state for 30 minutes followed by grinding in alcohol in a vibrating mill for 4 hours. The alcohol was evaporated and the magnetic powder worked up to form sintered pastils in the manner described in Example V. The pastils had the following properties:

Density (in g./cm. ³)	4.90
B _r (in Gauss)	3935
I ^H c (in Oersted)	1270
B ^H c (in Oersted)	1240
(BH) _{max} (in Gauss-Oersted)	2.90×10 ⁶

Example VIII

A magnetic powder was produced in the manner described in Example VII. This powder was mixed in a ball mill with 1% by weight of calcium carbonate; the mixture was then worked up to form sintered pastils in the manner described in Example IV. The sintered pastils had the following properties:

Density (in g./cm. ³)	4.93
B _r (in Gauss)	3590
I ^H c (in Oersted)	2190
B ^H c (in Oersted)	2040
(BH) _{max} (in Gauss-Oersted)	2.97×10 ⁶

Example IX

A magnetic powder was produced in the manner described in Example VII. The powder was then mixed

6

with 0.25% by weight of calcium carbonate and worked up to form sintered pastils in the manner described in Example II. The sintered pastils had the following properties:

Density (in g./cm. ³)	5.03
B _r (in Gauss)	4050
I ^H c (in Oersted)	1350
B ^H c (in Oersted)	1300
(BH) _{max} (in Gauss-Oersted)	2.90×10 ⁶

What is claimed is:

1. A method of manufacturing a permanent magnet having a (BH)_{max} value of more than 2.3×10^6 Gauss-Oersted comprising the steps, adding to a powdered mass consisting essentially of hexagonal crystals with a magnetoplumbite structure of a compound MO.6Fe₂O₃, in which M is a metal selected from the group consisting of barium, strontium and lead, as a recrystallization inhibitor, about 0.01 to 1% of an oxide selected from the group BaO, CaO, La₂O₃, Bi₂O₃, B₂O₃, As₂O₃ and Sb₂O₅, magnetically orienting said mass, forming said magnetically oriented mass into a body, and heating said body to a temperature of about 1150° C. to 1350° C. to form said permanent magnet.

2. A method of manufacturing a permanent magnet as claimed in claim 1 in which an atom fraction of not more than 0.4 of the metal M in said compound consists of calcium.

3. A method of manufacturing a permanent magnet as claimed in claim 1 in which the recrystallization inhibitor is La₂O₃.

4. A method of manufacturing a permanent magnet as claimed in claim 1 in which the recrystallization inhibitor is bismuth oxide.

5. A method of manufacturing a permanent magnet as claimed in claim 1 in which the recrystallization inhibitor is calcium oxide.

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