United States Patent [19]

Esper et al.

[11] **3,846,323**

[45] **Nov. 5, 1974**

[54] **PROCESS FOR MAKING A PERMANENT MAGNET MATERIAL**

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[22] Filed: **Aug. 25, 1972**

[21] Appl. No.: **283,702**

[30] **Foreign Application Priority Data**

Sept. 1, 1971 Germany 2143718

[52] **U.S. Cl.** **252/62.63**

[51] **Int. Cl.** **C04b 35/00**

[58] **Field of Search** 252/62.63

[56] **References Cited**

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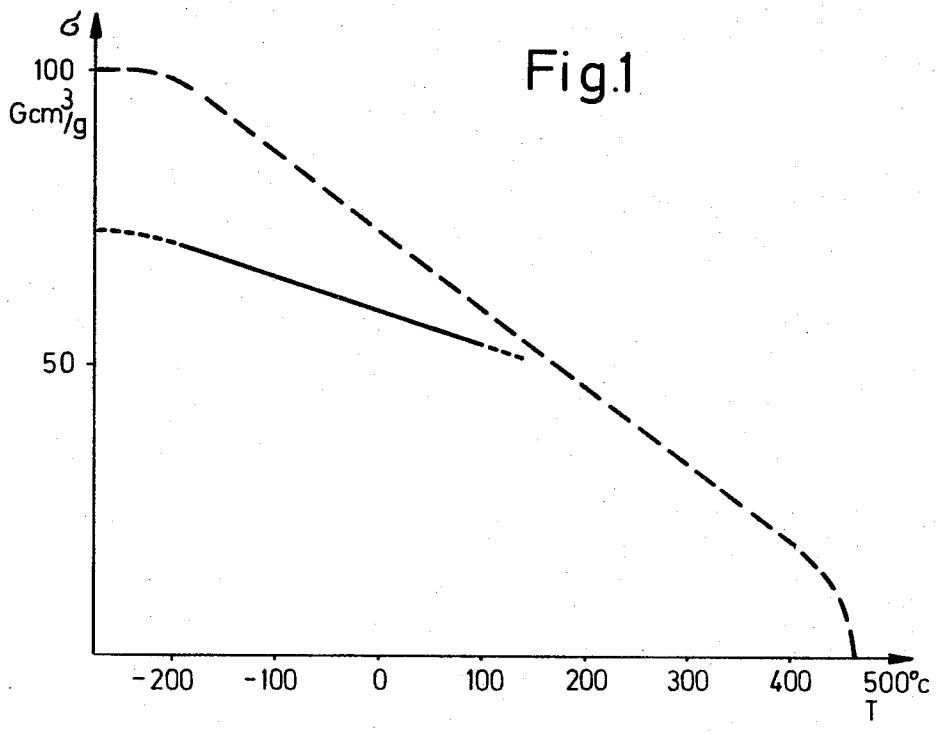
[57] **ABSTRACT**

A permanent magnet material comprises a ferrite of the elements barium, strontium or lead or a combination of these elements. The ferrite has a lattice structure of a strong uniaxial magnetic anisotropy and includes in its crystal structure a substitution element selected from the group consisting of Sb, As and P which has at least two valences of which the lowermost is 3 and which forms ions at both valences which have a radius substantially equal to or smaller than the radius of the Fe^{3+}–ions of the ferrite which ions are unable to form a ferromagnetic coupling and which are substituted in their trivalent form for at least part of said Fe^{3+} ions in at least one sublattice of said lattice structure.

The material is made by sintering a finely ground mixture of the oxides or oxide furnishing compounds, then heat-treating the sintered product in such a manner that it releases part of its oxygen and that the ions are being converted in the lattice structure of the ferrite into their trivalent form; then comminuting the product to single domain grain size and finally tempering it in a nonoxidising atmosphere.

5 Claims, 2 Drawing Figures

Fig.1


σ
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Gcm³/g
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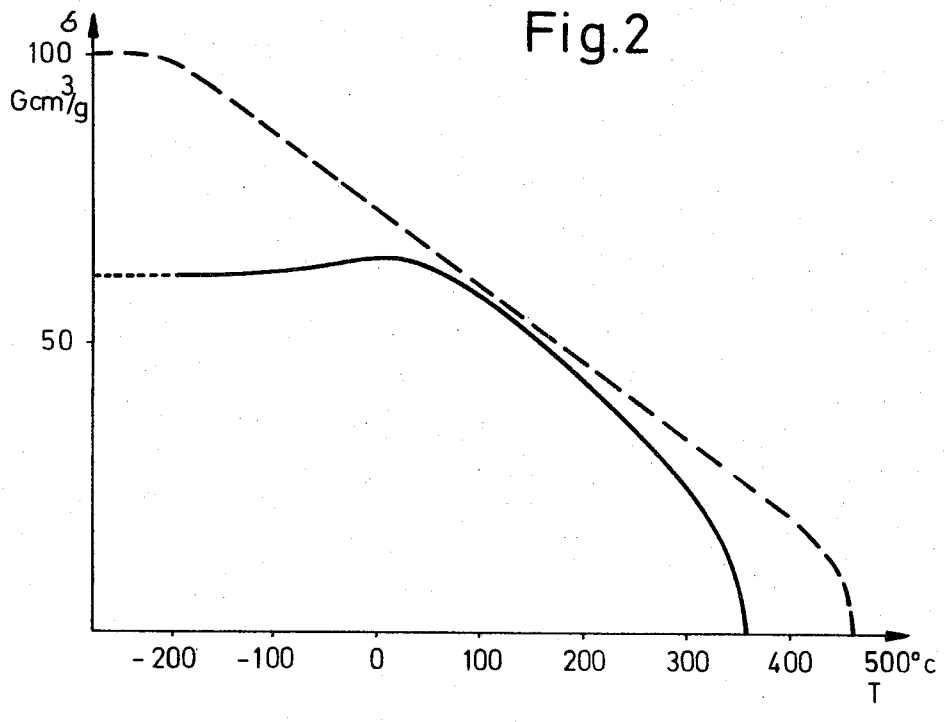
Fig.2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PROCESS FOR MAKING A PERMANENT MAGNET MATERIAL

BACKGROUND OF THE INVENTION

The invention relates to a permanent magnet material and a process of making it.

Some time ago a process has been proposed wherein by means of a substitution of titanium ions a reduced reversible temperature dependence of the magnetic saturation moment was to be accomplished (G. Heimke, in 'Berichte der Arbeitsgemeinschaft Ferromagnetismus 1959, Desseldorf 1960, p. 213–221, particularly p. 217 – 220). This process had a certain technical success. However it was accompanied by substantial decreases in the magnetic values such as the coercive force. Besides, limiting conditions were considered necessary regarding the chemical character of the substitution component, although these have later been shown to be unnecessary and even distracting from a useful solution. In all the proposition has not received acceptance in the industrial practice.

The object of the invention accordingly is to provide for a magnetic material and a process of making it wherein the material has a strong uniaxial magnetic anisotropy and assures a reversible temperature modification of the magnetic saturation moment.

SUMMARY OF THE INVENTION

The invention accordingly resides in a permanent magnet material which comprises a ferrite of the elements barium, strontium, or lead or a combination of these elements. The ferrite has a lattice structure of a strong uniaxial magnetic anisotropy and includes in its crystal structure a substitution element which has at least two valences of which the lowermost is **3** and which forms ions at both valences which have a radius substantially equal to or smaller than the radius of the Fe^{3+}–ions of the ferrite which ions are unable to form a ferromagnetic coupling and which are substituted in their trivalent form for at least part of said Fe^{3+} ions in at least one sublattice of said lattice structure.

The material is made by sintering a finely ground mixture of the oxides or oxide furnishing compounds, then heat-treating the sintered product in such a manner that it releases part of its oxygen and that the ions are being converted in the lattice structure of the ferrite into their trivalent form; then comminuting the product to single crystal grain size and finally tempering it in a nonoxidizing atmosphere.

BRIEF DESCRIPTION OF THE DRAWINGS

The drawings show interrelation of temperature and magnetic saturation moments in barium ferrites of the invention which are substituted in FIG. **1** with arsenic and in FIG. **2** with antimony and are compared with ferrites which are not substituted in this manner.

DESCRIPTION OF THE DETAILS OF THE INVENTION AND SPECIFIC EMBODIMENTS

The important points in the magnetic material of the invention include a substitution component which is constituted by an element, that has, at least two positive valences of which the lowermost valence is 3 while the higher valence or one higher valence preferably is 4 or 5. The radius of the ions of the element at both valences approaches the ion radius of the Fe^{3+}–ions.

Preferably it is smaller than or equal to the latter radius.

The mixture of the oxides used as starting products is first reacted by sintering in an oxidizing atmosphere and the product thus obtained is then subjected to a heat treatment in a suitable atmosphere for a time at a temperature to cause it to release part of its oxygen and to cause the ions of the substitution element to be converted in the crystal lattice of the ferrite into trivalent form. Following this heat treatment a fine grinding is effected to single domain grain size and this is followed by a tempering operation in a nonoxidizing atmosphere.

Even better results are obtained by again coarsely comminuting the product after the tempering treatment, grinding it, press forming a shaped body and drying the body.

The sintering operation may be effected at temperatures between 1,100° and 1,350°C for 1 hour and the heat-treating step may be carried out at a temperature between 1,200° and 1,350°C for 1 hour in air or nitrogen.

Preferred substitution components are compounds of the elements Sb, As or P. Preferably the substitution is made in a manner to cause 0.5 to 1 Fe^{3+}–ions to become substituted per molecular unit of ferrite. If the substitution is carried further a loss in the magnetic saturation moment will occur.

A heat treatment for removal of part of the oxygen preferably is effected in a manner to cause the product to release about ½ or 1 oxygen atom for each substituted Fe^{3+}–ion depending upon whether 1 or 2 valences become available upon change of the substituting ion from its higher valence.

The magnetic material of the invention permits to cause a lowering of the temperature coefficient α of the reversible temperature change of the magnetic saturation moment σ from the value $\alpha = 0.2$ percent/°C in normal Ba (Sr) ferrites to a value wherein α is about equal to 0.1 percent/°C or below such figure and in parts of the product even to ≈ 0. material. The is accomplished without reducing the magnetic value to a level which would exclude the usefulness of the oxide magnetic material saturation moment σ mentioned above is defined as follows:

$\sigma = I_S/\gamma$, wherein I_S = saturation magnetization,

γ = density; $-\alpha = ([\delta\sigma/\delta\tau]/\sigma 20°C.)$.

The accomplishment of the invention is illustrated by the drawings. FIG. **1** shows a barium ferrite substituted by arsenic as described in Example **1.** Its magnetic saturation moment is interrelated with the temperature, being indicated by the solid line, while the dashed line illustrates for a comparison a barium ferrite of the same type which however is not substituted by arsenic.

FIG. **2** is the same as FIG. **1** except that the barium ferrite in this case is substituted by antimony. The ferrite and the process of making it is described in Example **1.** The comparison barium ferrite is not substituted by antimony.

For making the product of the invention oxides of the various elements are used or compounds may also be employed instead which furnish oxides during the sintering step. However, the substitution element must comply with the specifications above given.

The components including the substitution element are then mixed in stoichiometric amounts as required by the intended final product. The mixture is subjected

to briquetting and in this form is sintered in air which causes a ferrite forming reaction. The briquettes are then crushed, the fragments are ground and the ground product is again subjected to briquetting.

This is followed by a heat treatment which regarding temperature, time and atmosphere employed must be adjusted to cause the sintered product to release the above-defined part of its oxygen. This oxygen removing treatment leads to some kind of equilibrium or at least close to such equilibrium where therefore a subsequent, similar and, in particular, nonoxidizing, treatment does not substantially affect the chemical or crystalline structure and characteristics of the product.

After the thermal treatment the product already has a crystal structure which is characterized by the decreased reversible temperature dependence of the magnetic saturation moment. It has however not yet a microstructure which permits to attain the optimum value of the coercive force ${}_IH_c$. For this reason a further treatment in two steps is preferred: (1) a fine grinding is effected to single domain range and (2) a tempering is carried out in a nonoxidizing atmosphere.

The tempering step is in any case necessary if the material resulting from the fine grinding is intended to form a magnetic body in which a synthetic binder is used. On the other hand if sintered shaped bodies are made from the material the sintering which is necessary in this connection will have the same effect. However it will in either case be a condition that a nonoxidizing atmosphere must be used.

The following examples will further illustrate the invention.

EXAMPLE 1

1. As substituted Ba-ferrite

The ferrite formed in this example has the empirical formula $BaO\ (As_2O_3)_{1/4}\ (Fe_2O_3)_5$, wherein one-half As ion is substituted in each molecular unit.

A mixture was formed of the following components:

	Weight %
$BaCO_3$	18.87
Fe_2O_3 (Farbenfabriken Bayer product "1640 HM")	76.40
As_2O_3	4.73

The oxides were mixed dry with about 0.5 percent by weight of cyclohexanone as grinding aid. The mixing was carried out for 15 minutes in a centrifugal pebble mill (Locke mill). The mass was then subjected to briquetting and sintered for 1 hour at 1,200°C in air. This was followed by crushing and wet grinding (in H_2O) for one-half hour in a pebble mill and finally drying and briquetting.

The product was then subjected to a heat treatment for 1 hour at 1,275°C in nitrogen.

The product obtained had the following specifications:

$\sigma = 58$ Gcm³/g, $\alpha = 0.1$ percent/°C, anisotropic field intensity

$H_A = 17{,}000$ Oe.

The product then was subjected to an aftertreatment consisting of a coarse comminution followed by wet grinding (in H_2O) for half an hour in a disk mill down to a grain size corresponding to 4 m²/g of specific surface.

The mass was then dried and a shaped body was formed by a pressing operation. The body was then subjected to renewed sintering for 1 hour at 1,100°C in nitrogen.

The coercive force of the final shaped body was as follows: ${}_IH_c = 1{,}550$ Oe.

The solid curve in FIG. 1 shows the magnetic saturation moment of the As substituted ferrite and the interrelation with the temperature while as above indicated the dashed curve shows the same relation for a non-substituted Ba ferrite.

EXAMPLE 2

2. Sb-substituted Ba ferrite.

Empirical formula: $BaO\ (Sb_2O_3)_{1/4}\ (Fe_2O_3)_5$, substitution one-half Sb-ion per molecular unit.

	Weight %
$BaCO_3$	18.47
Fe_2O_3 (Farbenfabriken Bayer product "1640 HM")	74.70
Sb_2O_3	6.83

Mixing: Dry with about 0.5 percent by weight cyclohexanone as grinding aid; 15 minutes in centrifugal pebble mill (Locke mill).

Briquetting

Sintering: 1 h, 1,200°C in air

Crushing

Grinding: wet (in H_2O), one-half h in pebble mill

Drying and briquetting

Thermal treatment: 1 h, 1,300°C in air (alternatively: 1 h, 1,200°C in nitrogen).

The thus obtained product had the following specifications:

$\sigma = 64$ Gcm³/g

$\alpha = 0.04$ percent/°C

Anisotropic field intensity $H_A = 6{,}500$ Oe

Crushing

Grinding: wet (in H_2O), 1 h in pebble mill to a grain size corresponding to 35 m²/g specific surface

Drying and forming of a shaped body

Sintering: 1 h at 750°C in nitrogen

Coercive force measured in the finished shaped body: ${}_IH_c = 700$ Oe

In FIG. 2 the solid curve shows the magnetic saturation moment of the Sb substituted Ba ferrite of the example. The dashed curve shows the corresponding value for a non-substituted Ba ferrite.

As appears from these two examples As and Sb have a different effect as substituents in that As reduces the temperature coefficient α only to one half but on the other hand permits to obtain higher values for the coercive force. Conversely, with Sb α is reduced almost by an order of magnitude and sometimes even more but with somewhat lower values for the coercive force.

EXAMPLE 3

As substituted Sr ferrite

Empirical formula: $SrO\ (As_2O_3)_{1/4}\ (Fe_2O_3)_5$, substituted by one-half As ion for each molecular unit.

Starting mixture:

	Weight %
$SrCO_3$	14.80
Fe_2O_3 (Farbenfabriken Bayer product "1640 HM")	80.25
As_2O_3	4.95

Mixing: dried with about 0.5 percent by weight of cyclohexane as grinding agent for 15 minutes in a centrifugal pebble mill (Locke mill)
Briquetting
Sintering for 1 h at 1,200°C in air
Crushing
Grinding: wet in H_2O for one-half h in a pebble mill

Drying and briquetting
Thermal treatment for 1 h at 1,325°C in nitrogen
Coarse comminution
Grinding: wet in H_2O for one-half h in disk mill to a grain size corresponding to 5 m^2/g of specific surface
Drying and making of a shaped body by pressing
Sintering: 1 h at 1,200°C in nitrogen
The thus obtained product had the following data:

$$\sigma = 69\ Gcm^3/g$$

$$\alpha = 0.1\ \text{percent/°C}$$

anisotropic field intensity $H_A = 17{,}500$ Oe
Coercive force measured in the final shaped body: ${}_iH_c = 1{,}750$ Oe.

EXAMPLE 4

P-substituted Ba ferrite
Empirical formula: $BaO\ (P_2O_5)_{1/4}\ (Fe_2O_3)_5$, substituent one-half P-ion per molecular unit.
Starting composition:

	Weight %
$BaCO_3$	19.11
Fe_2O_3 (Farbenfabriken Bayer product "1640 HM")	77.45
P_2O_5	3.44

Mixing: dry with about 0.5 percent by weight of cyclohexanone as grinding agent for 15 minutes in a centrifugal pebble mill (Locke mill)
Briquetting
Sintering for 1 h at 1,200°C in air
Crushing
Grinding: wet (in H_2O) for ½ h in a pebble mill
Drying and briquetting
Thermal treatment for 1 h at 1,325°C in nitrogen
Coarse comminution
Grinding: wet (in H_2O) for one-half h in disk mill to a grain size corresponding to 4 m^2/g of specific surface

Drying and making of a shaped body by pressing
Sintering for 1 h at 1,100°C in nitrogen.
The thus obtained product had the following data:

$$\sigma = 60\ Gcm^3/g$$

$$\alpha = 0.09\ \text{percent/°C}$$

anistropic field intensity $H_A = 16{,}500$ Oe
Coercive force measured in the shaped body ${}_iH_c = 700$ Oe.

EXAMPLE 5

Sb substituted Sr ferrit
Empirical formula: $SrO\ (Sb_2O_3)_{1/4}\ (Fe_2O_3)_5$, one-half Sb ion substituted per molecular unit.
Starting composition:

	Weight %
$SrCO_3$	14.45
Fe_2O_3 (Farbenfabriken Bayer product "1640 HM")	78.38
Sb_2O_3	7.17

Mixing: dry with about 0.5 percent by weight of cyclohexanone as grinding agent for 15 minutes in centrifugal pebble mill (Locke mill)
Briquetting
Sintering for 1 hour at 1,200°C in air
Crushing
Grinding: wet (in H_2O) for one-half h in a pebble mill

Drying and briquetting
Thermal treatment: 1 h at 1,350°C in nitrogen.
The thus-obtained product had the following data:

$$\sigma = 70\ Gcm^3/g$$

$$\alpha = 0.05\ \text{percent/°C}$$

anisotropic field intensity $H_A = 7{,}000$ Oe
Crushing
Grinding: wet (in H_2O) for 1 h in pebble mill to a grain size corresponding to 35 m^2/g of specific surface

Drying and making of a shaped body
Sintering for 1 h at 750°C in nitrogen
Coercive force measured in the finished shaped body ${}_iH_c = 750$ Oe.

Without further analysis, the foregoing will so fully reveal the gist of the present invention that others can by applying current knowledge readily adapt it for various applications without omitting features that, from the standpoint of prior art, fairly constitute essential characteristics of the generic or specific aspects of this invention and, therefore, such adaptations should and are intended to be comprehended within the meaning and range of equivalence of the following claims:

What is claimed as new and desired to be protected by Letters Patent is set forth in the appended claims:

1. A process of making a permanent magnet material, comprising the steps of forming a particulate mixture including a substance selected from the group consisting of the oxides and oxide furnishing compounds of Fe, a substance selected from the group consisting of the oxides and oxide furnishing compounds of Ba, Sr and Pb, and a substance selected from the group consisting of the oxides and oxide furnishing compounds of Sb, As and P; sintering said mixture in air so as to effect reaction of said substances and form a first product of the formula $MO{\cdot}(Fe_2O_3)_6$ wherein Fe^{+3} ions in said first product are replaced by the ions of at least one of said Sb, As and P to such an extent as to cause a lowering of the temperature coefficient of the reversible temperature change of the magnetic saturation moment from that of $MO{\cdot}(Fe_2O_3)_6$ wherein no replacement of the Fe^{+3} ions is effected, said ions of said Sb, As and P having a valence in excess of +3, and said M of said $MO{\cdot}(Fe_2O_3)_6$ being at least one of said Ba, Sr and Pb; heat treating said first product within a temperature range of 1,200° to 1,350°C so as to cause evolution of part of the oxygen of said first product and so as to convert said ions of Sb, As and P to their trivalent state thereby forming a second product; comminuting said second product to single domain size; and tempering the comminuted second product in a non-oxidizing atmosphere within a temperature range of 750° to 1,200°C.

2. A process as defined in claim 1, wherein at least 0.5 Fe^{+3} ions are replaced by said Sb, As and P per molecular unit of $MO \cdot (Fe_2O_3)_6$.

3. A process as defined in claim 1, wherein approximately 1 atom of said oxygen is evolved per replaced Fe^{+3} ion.

4. A process as defined in claim 1; further comprising the step of press forming the comminuted second product into a shaped body prior to said tempering step; and wherein said tempering step comprises sintering said shaped body.

5. A process as defined in claim 1, wherein said sintering step is carried out at a temperature between substantially 1,100° and 1,350°C.

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