Jan. 31, 1961

A. PIERROT ET AL

FERROMAGNETIC MATERIALS WITH RECTANGULAR HYSTERESIS CYCLE AND METHOD FOR THEIR MANUFACTURE

2,970,112

Filed April 10, 1956

4 Sheets-Sheet 1

Fig. 1

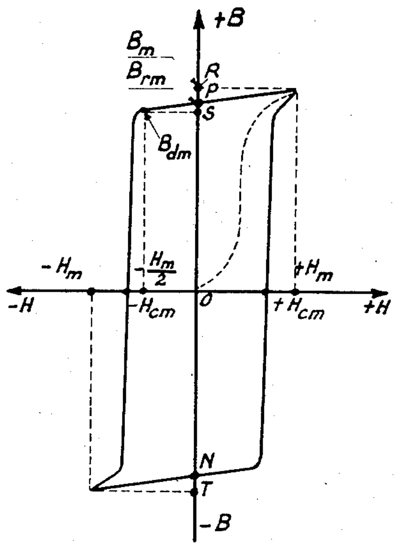
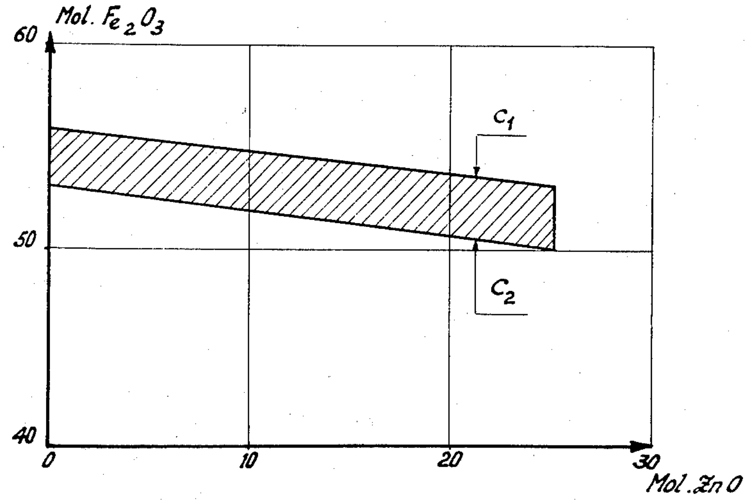


Fig. 2



Jan. 31, 1961

A. PIERROT ET AL

FERROMAGNETIC MATERIALS WITH RECTANGULAR HYSTERESIS CYCLE AND METHOD FOR THEIR MANUFACTURE

2,970,112

Filed April 10, 1956

4 Sheets-Sheet 2

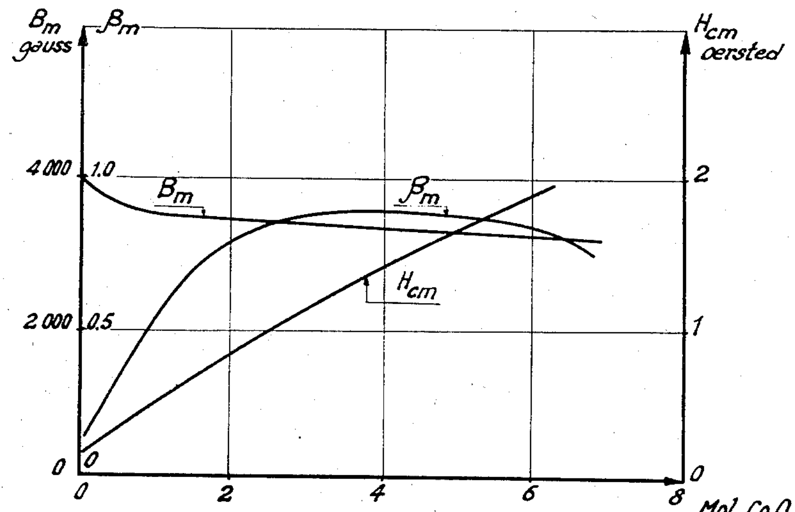


Fig. 3

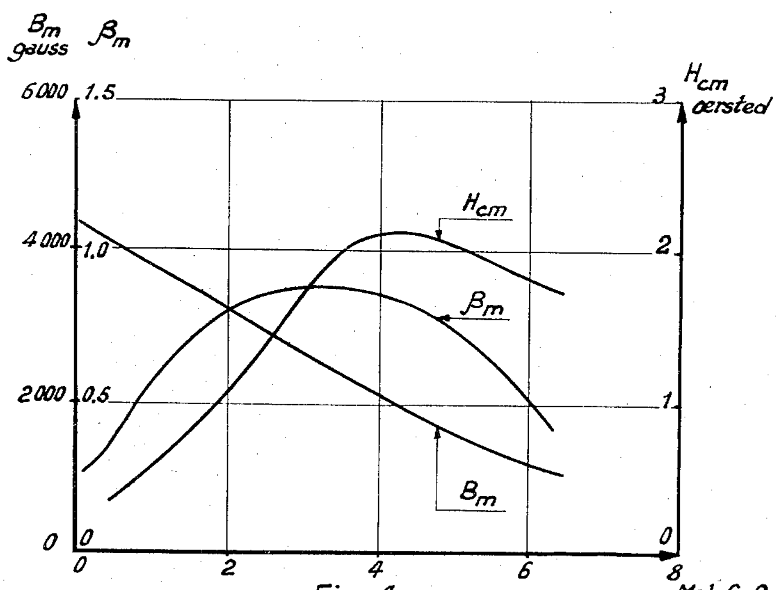


Fig. 4

Jan. 31, 1961

A. PIERROT ET AL

2,970,112

FERROMAGNETIC MATERIALS WITH RECTANGULAR HYSTERESIS CYCLE AND METHOD FOR THEIR MANUFACTURE

Filed April 10, 1956

4 Sheets-Sheet 3

Fig. 5

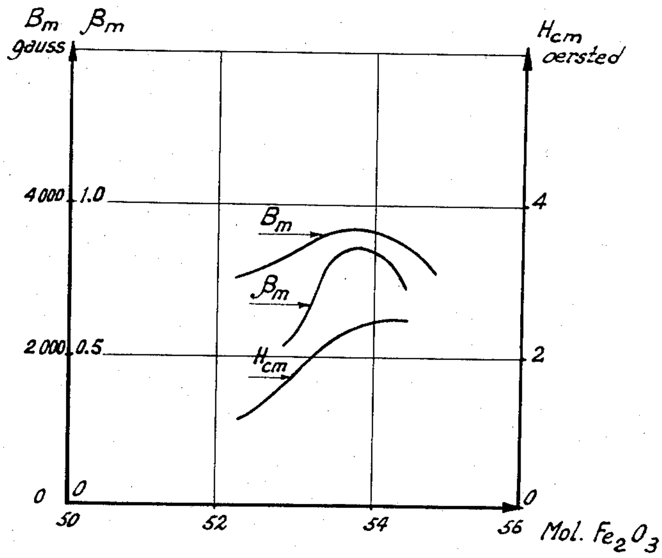


Fig. 6

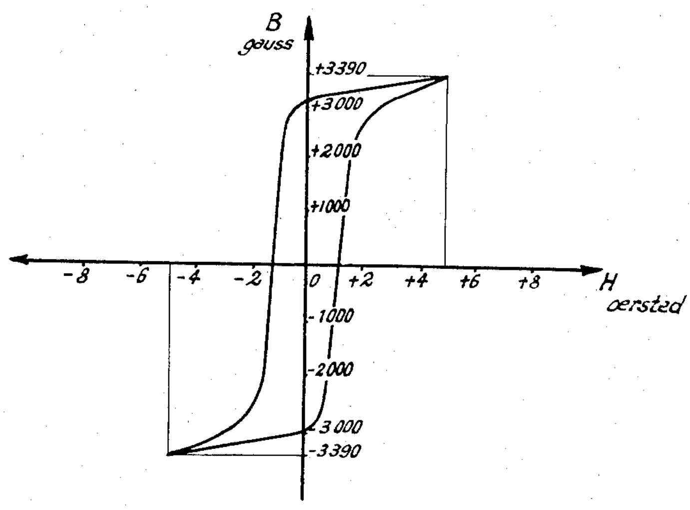


Fig. 7

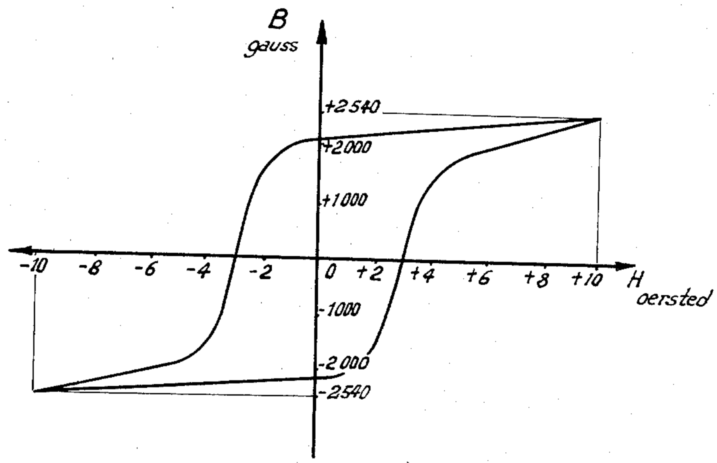
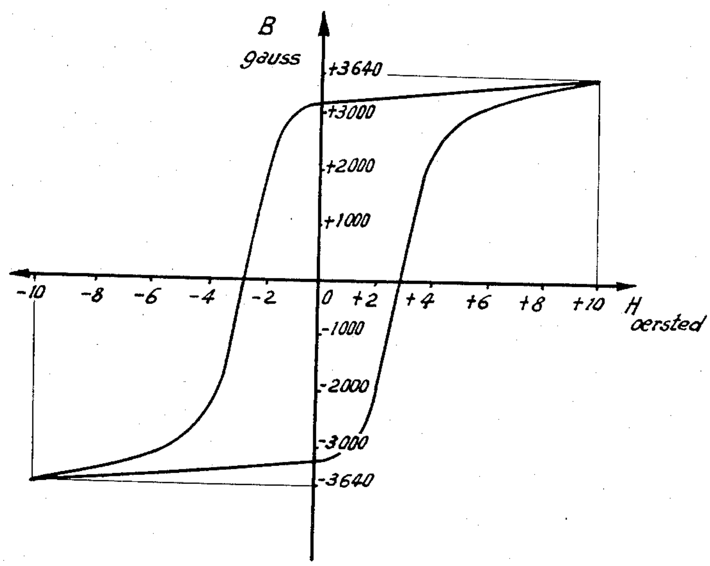

B
gauss
+2540
+2000
+1000
-10
-8
-6
-4
-2
0
+2
+4
+6
+8
+10
H
oersted
-1000
-2000
-2540

Fig. 8


B
gauss
+3640
+3000
+2000
+1000
-10
-8
-6
-4
-2
0
+2
+4
+6
+8
+10
H
oersted
-1000
-2000
-3000
-3640

United States Patent Office

2,970,112

Patented Jan. 31, 1961

1

2,970,112

FERROMAGNETIC MATERIALS WITH RECTANGULAR HYSTERESIS CYCLE AND METHOD FOR THEIR MANUFACTURE

André Pierrot, Yves C. E. Lescroel, and Bogdan Grabowski, all of Conflans Ste.-Honorine, France, assignors to Lignes Telegraphiques and Telephoniques, Paris, France

Filed Apr. 10, 1956, Ser. No. 577,327

Claims priority, application France May 3, 1955

8 Claims. (Cl. 252—62.5)

This invention relates to ferromagnetic materials of the ferrite type, having substantially rectangular hysteresis cycles, and to their manufacture methods.

Such materials can be employed in magnetic recording devices known as "memory devices," magnetic control members, magnetic amplifiers and the like. In these applications, materials according to the invention are generally used in the form of toroidal cores or at least of closed magnetic circuits without air-gap.

Materials with a hysteresis cycle of rectangular shape are already known, particularly alloys of iron and nickel or of iron and silicon, the magnetic properties of which are most frequently rendered anisotropic either by cold rolling or by heat treatment under a magnetising field. These materials, generally speaking, have high saturation flux density and low coercive fields.

The great drawback of these metallic materials, despite their usually high saturation flux density, is the low value of their resistivity, which leads to considerable eddy-current losses. These high losses result in an increase of the response time and an alteration of the hysteresis cycle, which then loses its character of rectangularity as soon as the operating frequency increases. If it be desired to employ these materials at several megacycles per second, they must be obtained in very thin sheets with a thickness of the order of a few microns, and their price immediately becomes prohibitive.

Before the present invention is explained, some definitions will be given of the characteristics relating to the hysteresis cycles and other magnetic characteristics which will be used.

A substantially rectangular hysteresis cycle, plotted for a magnetising field practically reaching saturation is defined in the following terms:

B_s: saturation magnetic flux density in gauss;
B_r: residual or remanent magnetic flux density in gauss;
H_c: coercive field in oersteds;

$\beta=\frac{B_r}{B_s}$: ratio of remanent flux density to saturation flux density.

Furthermore, the following terms may be used in connection with a work cycle in which the field varies between a maximum positive value H_m and a maximum negative value $(-H_m)$;

B_m: flux density when the field has the value H_m, in gauss;
B_{rm}: residual or remanent flux density, in gauss;
H_{cm}: coercive field, in oersted;

$\beta_m=\frac{B_{rm}}{B_m}$: coefficient of rectangularity;

B_{dm}: final value of the flux density when the magnetising field varies from a value H_m, comprised between H_{cm} and $2H_{cm}$, to the value

$$\left(-\frac{H_m}{2}\right)$$

$R_m=\frac{B_{dm}}{B_m}$: ratio of rectangularity.

It is also possible, in some cases, to evaluate the slopes of the substantially vertical and horizontal sides of the hysteresis cycle.

The quantities:

$$P_h=\left(\frac{\Delta B}{\Delta H}\right)_h$$

and

$$P_v=\left(\frac{\Delta B}{\Delta H}\right)_v$$

in which ΔB and ΔH are small variations of the flux density and of the magnetising field in the vicinity of a given point, are respectively the slope of the curve representing the hysteresis cycle when the field passes through zero and the slope of the curve when the flux density passes through zero.

For an ideal rectangular cycle, the respective values of P_h and P_v would tend towards unity and infinity; the coefficient of rectangularity β_m and the ratio of rectangularity R_m would tend towards unity.

The magnetic permeability μ is defined as the initial permeability in the demagnetised state.

The coefficient of eddy-current losses F_n, expressed in ohms per henry, referred to the frequency of 800 cycles per second is measured between 100 and 200 kilocycles per second, for a field of 2 millioersteds and at a temperature of about 20° C. for the circuits, the cross-section of which is about 0.3 square centimeter.

The magnetostrictive effect may be defined by the value of the coefficient of magnetostriction at saturation λ_s, which is obtained by extrapolating, for the demagnetised state, the curve of relative variation $\Delta l/l$, in the applied field direction, of the length l of the sample, versus this field, plotted for very high field strengths.

The "response time" is defined by considering two windings, having negligible time constant, placed on a core made of the magnetic material concerned; this core is subjected to the magnetising field having the value H_m, comprised between H_{cm} and $2H_{cm}$, and then to a field having the value

$$\left(-\frac{H}{2}\right)$$

a current pulse the rising time of which is very short (for example, less than 0.1 microsecond) is applied to one of the windings and causes the magnetising field to pass to the value $(-H_m)$, the "response time" τ is the time, expressed in microseconds, necessary for the voltage produced in the other winding, starting from zero, to pass through a maximum and return to 10% of the value of this maximum.

The object of the invention is to provide magnetic materials of the ferrite type having on the one hand: substantially rectangular hysteresis cycles with a coefficient of rectangularity β_m at least equal to 0.80; and on the other hand: high electrical resistivities ρ at least equal to 10^6 ohms-cm., low eddy-current loss coefficient F_n at most equal to 0.20.

The rectangularity of the cycle is obtained by starting from materials of the ferrite type with a negative magnetostriction coefficient, which are subjected to strains developed during a heat treatment by means of which a considerable linear shrinkage is produced, of at least 8%, and which may go up to 30%, this being one of the characteristics of the method of the invention.

In view of their high resistivity, these materials have negligible eddy-current losses, which makes it possible to use them at high frequency with very low response times τ at most equal to 5 microseconds.

The materials according to the invention have inductions at saturation B_s of the order of 2,500 to 4,500 gauss, at about 20° C., coercive fields H_c comprised between 1 and 4 oersteds, and "coefficients of rectangularity" β_m greater than 0.80.

The invention provides a method of manufacture of ferromagnetic materials of the ferrite type having a substantially rectangular hysteresis cycle, comprising preparing a homogeneous mixture of fine powders of ferric oxide, with oxides of manganese and cobalt, and if desired oxide of zinc; the molecular proportions of the various oxides in the mixture respectively being 50 to 56% for the ferric oxide; 22 to 47% for the manganese and cobalt oxides and 0 to 25% for the oxide of zinc; the ferric oxide varying between 53 and 56% when no zinc oxide is present and between 50 and 53% when 25% zinc oxide is used. The method further comprises the steps of compressing the mixture into cores and heat treating at a temperature between 1200° C. and 1300° C. in a nitrogen atmosphere containing a small percentage of oxygen, followed by slow cooling carried out in an inert atmosphere.

In the above description it must be understood that the molecular percentage of manganese oxide is conventionally referred to the number of atoms of manganese; consequently, in the following description the manganese oxide will be conventionally represented by MnO, although, in practice, it is possible to use different oxides such as MnO_2, Mn_3O_4, and so forth.

It should be noted that the above mixture necessarily comprises a hardening element. By "hardening" element is meant any oxide of bivalent metal capable of forming with an oxide of trivalent metal, more particularly with iron oxide, a ferrite with a magnetostrictive coefficient of relatively high but negative value and, if necessary, modifying in an appreciable manner the constant of anisotropy K of the relatively soft ferrite in which it is in solution.

The invention will be more particularly described in the following on ferrites prepared from mixtures whose starting compositions correspond to the formula

$$x\mathrm{Fe_2O_3},\ u\mathrm{MnO},\ v\mathrm{CoO},\ s\mathrm{ZnO}$$

where x, u, v and s are the molecular percentages which satisfy the following relations

$$x+u+v+s=100$$

$$50\leq x\leq 56$$

$$22\leq u+v\leq 47$$

$$0\leq s\leq 25$$

and

$$1\leq v\leq 6$$

The Curie points θ_c, of the final product obtained, are always higher than 150° C.

In all the following description of the present invention, the compositions indicated are starting compositions before the mixture of oxides is reduced to powder by grinding. The increase in the iron content, due to the wear of the grinder, being for an average grinder about 0.8 molecule Fe_2O_3 per hundred molecules of ground material, the percentages of Fe_2O_3 indicated after grinding have to be increased by this quantity in order to obtain the percentages of Fe_2O_3 after grinding. Corrections would have to be made if a grinder were used which wore out more slowly or more quickly.

According to the invention, in a relatively soft ferrite containing iron, manganese and, if desired, zinc, cobalt oxide may be substituted for a portion of the manganese oxide.

The relatively soft ferrites in which the substitution mentioned above is made, have a practically zero magnetostriction coefficient λ_s. In a ferrite of manganese-zinc for which λ_s is zero, it is necessary for a certain quantity of ferrous iron to be formed so that the ferrite Fe_3O_4 may have a sufficient positive magnetostriction coefficient to cancel those of the other ferrites.

In the circumstances, the presence of a certain quantity of cobalt oxide makes possible the formation of the ferrite of cobalt which, in view of the treatment comprising slow cooling, has a definitely negative coefficient of magnetostriction.

It follows, on the one hand, that the constant of anisotropy of the ferrite is substantially increased, which results in an increase of the coercive field H_c.

The formed ferrite has, on the other hand, a definitely negative magnetostriction coefficient which is a necessary condition in order that, after suitable treatment and determined consecutive shrinkage, it may have a substantially rectangular hysteresis cycle.

It has, moreover, been noticed that the resistivity of the material is greatly increased and that the coefficients of eddy-current losses are lower than 0.20, very often even less than 0.10.

The relatively high iron content has two interesting consequences: on the one hand, an increase of the Curie point θ_c and a better stability of the characteristics as a function of the temperature, and on the other hand, the saturation flux density is rather high, usually reaching values comprised between 2,500 and 4,500 gauss.

The invention will be described in more detail hereafter particularly with reference to exemplary embodiments and to the attached drawings, in which:

Figure 1 represents a practically rectangular hysteresis cycle.

Figure 2 represents the molecular percentages of ferric oxide, as a function of the molecular percentages of zinc oxide, of a material in accordance with the invention.

Figure 3 represents the characteristics of a material, in accordance with the invention, as a function of its content of cobalt oxide.

Figure 4 represents the same characteristics in a material of another composition.

Figure 5 represents the characteristics for another material as a function of its content of ferric oxide.

Figures 6, 7 and 8 respectively represent the hysteresis cycles corresponding to materials of different compositions.

In Figure 1 which represents a rectangular hysteresis cycle corresponding to a field H_m, the flux density $B_m=OR$, the remanent flux density $B_{rm}=OP$, the flux density $B_{dm}=OS$ corresponding to a magnetising field

$$\left(-\frac{H_m}{2}\right)$$

and the coercive field H_{cm} are indicated.

For the "coefficient of rectangularity" there is

$$\beta_m=\frac{B_{rm}}{B_m}=\frac{OP}{OR}$$

for the "ratio of rectangularity"

$$R_m=\frac{B_{dm}}{B_m}=\frac{OS}{OR}$$

It should be noted that if $\beta_m=1-\alpha$, there is

$$R_m\leq 1-\frac{3\alpha}{2}$$

The respective proportions of iron, manganese and cobalt in the mixture of oxides used in the preparation of a material in accordance with the invention are rather critical; especially for a particular content of zinc oxide, the content of ferric oxide must not differ from the optimum value by more than 3%. On the diagram of Figure 2, in which the content s of zinc oxide is plotted as abscissa and the content x of ferric oxide as ordinate, a hatched zone is shown limited by the two curves C_1 and C_2; the points inside this zone indicate the contents of ferric oxide to be introduced into the starting mixture of oxides for a predetermined content of zinc oxide.

Figure 2 shows that when the molecular percentage of zinc oxide is of the order of 20%, the most suitable molecular percentage of ferric oxide is close to 52.5%, while it should be about 54% when there is no zinc oxide. This optimum content of ferric oxide may vary slightly according to the molecular percentage of cobalt oxide which is present; in any case, the possible scope of variation of the molecular percentage of ferric oxide available is approximately 3%.

Figures 3 and 4 show the influence of the substitution of a certain number of CoO molecules for an equal number of MnO molecules upon the characteristics of β_m, H_{cm}, B_m for a cycle corresponding to a field H_m of 5 oersteds.

Figure 3 shows, for example, that β_m passes through a maximum for the composition:

52.5% Fe_2O_3, 28.3% MnO, 19.2% ZnO

when 4 CoO molecules are substituted therein for 4 MnO molecules. Then, the maximum value of β_m is near 0.90.

In Figure 4, the same characteristics B_m, H_{cm}, β_m taken for a cycle corresponding to a field H_m of 5 oersteds, are plotted as a function of the content of CoO molecules which have been substituted for an equal quantity of MnO molecules in the ferrite prepared from a mixture of the following composition:

54% Fe_2O_3, 38% MnO, 8% ZnO

It will be seen that β_m passes through a maximum for a content of CoO molecules equal to 3%, the maximum value of β_m being near 0.86.

The curves of Figure 5 represent as a function of the content x of Fe_2O_3, the variations of the characteristics B_m, H_{cm}, β_m for starting compositions comprising constant contents of cobalt oxide and zinc oxide and respectively equal to 4% and 10%; the maximum of β_m is equal to 0.87 and occurs for a value of x equal to 53.5; the curve for β_m is rather sharp and β_m is higher than 0.80 for x comprised between 53.3 and 54.2; the flux density corresponding to a field H_m of 10 oersteds passes through a maximum at the same time as β_m.

METHOD OF MANUFACTURE

Composition and nature of oxides employed

For the mixtures, ferric oxide (Fe_2O_3), saline oxide of manganese (Mn_3O_4), oxide of cobalt (CoO) and oxide of zinc (ZnO) are used.

These oxides must be pure and the mixture must not contain more than 0.5% of impurities. By impurities are meant products such as silica (SiO_2), sulphur, alkali metals (Na, K), and so forth.

The "black" industrial cobalt oxide must be preliminarily treated, at 900° C., in order to eliminate its impurities and its humidity, and to bring it to a state near CoO.

Grinding

The mixture of oxides is ground or milled in an appropriate device such as an iron grinder, with steel balls, usually for 12 to 48 hours, with a weight of distilled water equal to about twice the weight of the mixture.

Pressing

The influence of the pressure exerted in the pressing operation is considerable. It must be sufficiently great for the induction at saturation of the finished product to be

sufficiently high, and on the other hand, sufficiently low, for the shrinkage during sintering to be considerable.

A pressure of about 5 tons per square centimeter, which corresponds to linear shrinkages of about 15%, has given good results; it is possible, however, to go from 0.5 to 15.0 tons per square centimeter.

Heat treatment

The product so obtained is subjected to a heat treatment consisting of a heating lasting from 2 to 6 hours at a temperature comprised between 1,200° C. and 1,300° C. in a mixture of pure nitrogen and of 0 to 2% in volume of oxygen, followed by slow cooling carried out for about 15 hours in pure nitrogen.

In order to obtain the optimum properties, the temperature and atmosphere of the annealed products must be experimentally adjusted for each composition.

EXAMPLES

The following examples show the characteristics of a certain number of materials obtained according to the invention.

Example 1

Figure 6 represents the hysteresis cycle taken in direct current for a maximum magnetising field H_m of 5 oersteds on a toroidal ferrite core having the following dimensions:

	Millimeters
Outer diameter	28.0
Inner diameter	15.0
Height	5.4

The starting composition of the material corresponded to the formula in molecular percentage:

52.5% Fe_2O_3, 23.3% MnO, 5.0% CoO, 19.2% ZnO

The grinding was carried out for 48 hours in an iron mill with a capacity of 16 litres, containing about 3 kg. of mixture, about 6 litres of water and about 20 kilograms of steel balls of different dimensions.

The annealing was carried out at 1,240° C., for four hours, in a mixture of pure nitrogen and of 1% of oxygen in volume, and cooling took place in pure nitrogen.

This material shows, for a cycle corresponding to a field H_m of 5 oersteds, the following characteristics:

Coercive field H_{cm}	oersteds	1.55
Maximum flux density B_m	gauss	3,390
Coefficient of rectangularity β_m		0.87
P_h		50
P_v		5,000
Initial permeability μ		93
Coefficient of eddy-current losses F_n		0.03

This very low coefficient of eddy-current losses ensures the stability of the hysteresis cycle as a function of the frequency, and a preservation of the characteristics indicated, as a function of the frequency, up to very high values; consequently, it renders the response time very short. This is also one of the characteristics of the invention.

Example 2

Figure 7 represents the hysteresis cycle taken in direct current for a maximum magnetising field H_m of 10 oersteds, on a toroidal ferrite core, the dimensions of which are as follows:

	Millimeters
Outer diameter	34.5
Inner diameter	27.3
Height	5.4

The starting composition of the material corresponded to the following formula in molecular percentage:

54% Fe_2O_3, 41% MnO, 5% CoO

This material has been treated in accordance with the same process as that of Example 1.

It has a shrinkage of 13.8% and shows the following properties:

Maximum flux density B_m	gauss	2,540
Coercive field H_{cm}	oersteds	3
Coefficient of rectangularity β_m		0.83
Coefficient of eddy-current losses F_n		≤0.001
Initial permeability μ		35

Example 3

Figure 8 represents the hysteresis cycle taken with direct current for a maximum magnetising field H_m of 10 oersteds on a toroidal ferrite core of the following dimensions:

	Millimeters
Outer diameter	34.4
Inner diameter	27.4
Height	11.2

The starting composition of the material corresponded to the following formula in molecular percentage.

53.5% Fe_2O_3, 32.5% MnO, 4% CoO, 10% ZnO

this material has been treated in accordance with the same process as that in Example 1.

It has a shrinkage of 14.0% and shows the following properties:

Maximum flux density B_m	gauss	3,640
Remanent flux density B_{rm}	do	3,180
Coefficient of rectangularity β_m		0.87
P_h		50
P_v		4,000
Initial permeability μ		58
Coefficient of eddy-current losses F_n		≤0.001

The following corresponds to a working field H_m of 4 oersteds:

Maximum flux density B_m	gauss	2,420
Remanent flux density B_{rm}	do	2,020
Coefficient of rectangularity β_m		0.84
Ratio of rectangularity R_m		0.52

There will now be obvious to those skilled in the art many modifications and variations utilizing the principles set forth and realizing many or all of the objects and advantages of what has been described but which do not depart essentially from the spirit of the invention.

What is claimed is:

1. A process for producing ferromagnetic materials of the ferrite type with a rectangular hysteresis cycle such that the ratio of remanent flux density to maximum flux density is at least 0.80 for a maximum magnetising field between 5 and 10 oersteds, comprising compressing a homogeneous mixture of fine powders of metallic oxides and subjecting the mixture so compressed to a heat treatment carried out for 2 to 6 hours at a temperature between 1,200 and 1,300° C. in pure nitrogen with the addition of 0 to 2% by volume of oxygen, slowly cooling the compressed mixture for about 15 hours in an inert atmosphere, the said mixture being composed of ferric oxide, of manganese and cobalt oxides and oxide of zinc wherein in the said mixture the sum of the molecular percentage of the manganese oxide, conventionally related to the number of atoms of manganese and the percentage of cobalt oxide is between 22 and 47%, the molecular percentage of cobalt oxide is between 1 and 6%, the molecular percentage of zinc is between 0 and 25% and the molecular percentage of ferric oxide is between 50 and 56%, said ferric oxide varying between 53 and 56% when the zinc oxide is 0% and between 50 and 53% when 25% zinc oxide is used, the relationship of the ferric oxide to the zinc oxide varying linearly between these values.

2. A process according to claim 1, wherein the molecular percentages of the said ferric oxide, cobalt oxide and manganese oxide are respectively equal to 54, 5 and 41.

3. A process according to claim 1, wherein the molecular percentages of the said ferric oxide, cobalt oxide, zinc oxide and manganese oxide are respectively equal to 52.5, 5, 19.2 and 23.3.

4. A process according to claim 1, wherein the molecular percentages of the said ferric oxide, cobalt oxide, zinc oxide and manganese oxide are respectively equal to 53.5, 4, 10 and 32.5.

5. A ferromagnetic body of a ferrite type resulting from the process of compressing a homogeneous mixture of fine powders of metallic oxides and subjecting the mixture so compressed to a heat treatment carried out for 2 to 6 hours at a temperature between 1,200 and 1,300° C. in pure nitrogen with the addition of 0 to 2% by volume of oxygen, slowing cooling the compressed mixture for about 15 hours in an inert atmosphere, the said mixture being composed of ferric oxide, of manganese and cobalt oxides and oxide of zinc wherein in the said mixture the sum of the molecular percentage of the manganese oxide, conventionally related to the number of atoms of manganese and the percentage of cobalt oxide is between 22 and 47, the molecular percentage of cobalt oxide is between 1 and 6, the molecular percentage of zinc is between 0 and 25 and the molecular percentage of ferric oxide is between 50 and 56%, said ferric oxide varying between 53 and 56% when the zinc oxide is 0% and between 50 and 53% when 25% zinc oxide is used, the relationship of the ferric oxide to the zinc oxide varying linearly between these values whereby there is produced a rectangular hysteresis cycle such that the ratio of remanent flux density to maximum flux density is at least 0.80 for a maximum magnetising field between 5 and 10 oersteds.

6. A ferromagnetic material according to claim 5, wherein the molecular percentages of the said ferric oxide, cobalt oxide and manganese oxide are respectively equal to 54, 5 and 41.

7. A ferromagnetic material according to claim 5, wherein the molecular percentages of the said ferric oxide, cobalt oxide, zinc oxide and manganese oxide are respectively equal to 52.5, 5, 19.2 and 23.3.

8. A ferromagnetic material according to claim 5, wherein the molecular percentages of the said ferric oxide, cobalt oxide, zinc oxide and manganese oxide are respectively equal to 53.5, 4, 10 and 32.5.

References Cited in the file of this patent

UNITED STATES PATENTS

2,179,810	Brill et al.	Nov. 14, 1939
2,535,025	Albers-Schoenberg	Dec. 26, 1950
2,551,711	Snoek et al.	May 8, 1951
2,565,861	Leverenz et al.	Aug. 28, 1951
2,579,978	Snoek et al.	Dec. 25, 1951
2,626,445	Albers-Schoenberg	Jan. 27, 1953
2,636,860	Snoek et al.	Apr. 28, 1953
2,715,109	Albers-Schoenberg	Aug. 9, 1955
2,723,239	Harvey	Nov. 8, 1955
2,882,236	Gorter et al.	Apr. 14, 1959
2,886,529	Guillaud	May 23, 1959

FOREIGN PATENTS

1,033,268	France	Apr. 1, 1953
1,086,346	France	Aug. 11, 1954
1,093,965	France	Dec. 1, 1954
1,117,385	France	Feb. 20, 1956

OTHER REFERENCES

Philips Technical Review, vol. 16, No. 2, August 1954, pages 49–58.