June 6, 1961 J. M. BROWNLOW 2,987,481

MANGANESE-ZINC FERRITE

Filed Oct. 15, 1956

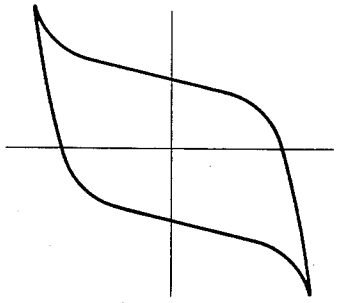


FIG.1c

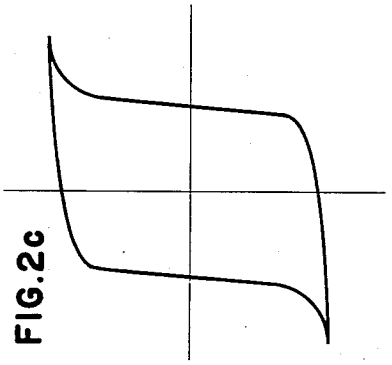


FIG.2c

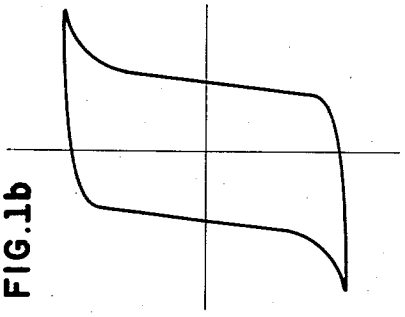


FIG.1b

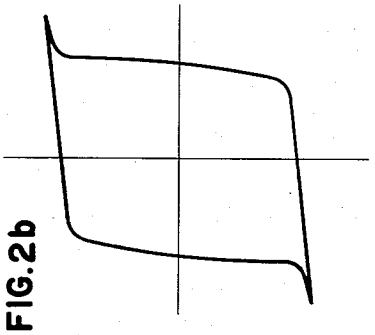


FIG.2b

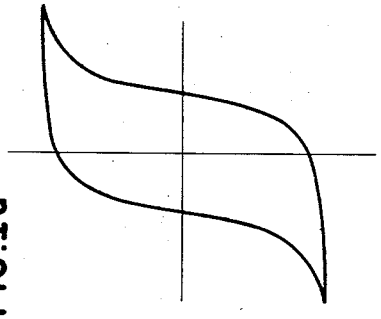


FIG.1a

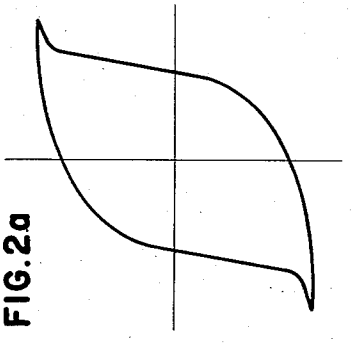


FIG.2a

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MANGANESE-ZINC FERRITE

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This invention relates to magnetic materials of the spinel type generally known as ferrites or ferrospinels and is directed particularly to an improved method for producing bodies of such materials so as to exhibit maximum squareness of the hysteresis characteristic.

Ceramic ferrite bodies are widely employed as magnetic memory elements and pulse transfer controlling devices in computers and other information processing systems and in this environment the degree of squareness of the hysteresis loop is desirably high for optimum performance.

Ferrospinels are generally synthesized by mixing selected constituent metallic oxides in predetermined proportions, pressing the mixture into rigid shapes and thereafter heating the pressed material to a high temperature. During the interval that the intimately mixed oxide components are subjected to the high temperature they react and diffuse on an atomic and molecular scale to form a spinel type crystal structure.

A primary objective of the present invention is to provide an improved heat treating technique that causes the material to form a heterogeneous solution of such a nature that the ferrite body demonstrates a maximum degree of squareness. This is obtained when the temperature to which the mixture is heated is such as to develop crystal grains of a first chemical phase, with the ferrite body then cooled to a temperature where reoxidation can occur and cause the development of a second chemical phase. When this new phase is controlled so as to develop only within the skin of the shaped body, a substantial improvement in loop squareness is obtained.

This reoxidation process may be accomplished by introducing an oxygen containing atmosphere surrounding the material during the aforementioned heating interval while cooling the body from the sintering temperature to a lower temperature conducive to formation of the second phase. Alternatively, the body may be retained in the initial chemical phase as a solid solution by quenching from the high sintering temperature and thereafter the heterogeneous solution may be produced by causing the second chemical phase to develop through refiring at a particular annealing temperature for a predetermined time. In either case, the initial firing may be carried out in air or in a neutral gas as desired.

Accordingly, one object of the invention is to provide an improved heat treatment process for ferrites including a controlled reoxidation step which, when properly modified for each ferrite composition, yields improved hysteresis loop squareness due to development of a second chemical phase.

Another object of the invention broadly is to improve the pulse performance of ferrite cores when used as memory elements. In this regard, binary information is represented by the opposite conditions of remanence attained by a magnetic body and when such a memory element is interrogated by applying a magnetomotive force tending to establish one of these states as a datum condition, the signal ratio is higher when the squareness of the hysteresis characteristic is more nearly ideal.

Still another object of the invention is to provide an improved magnetic memory element through formation of a second chemical phase within the skin region of the element.

A more specific object of the invention is to provide an

improved process for the heat treatment of ferrites whereby iron oxide in the body centered crystalline form of α-Fe_2O_3 is developed in the skin region of the elements to a predetermined degree of concentration and depth penetration.

Other objects of the invention will be pointed out in the following description and claims and illustrated in the accompanying drawings, which disclose, by way of example, the principle of the invention and the best mode, which has been contemplated, of applying that principle.

In the drawings:

FIGURES 1*a*, 1*b* and 1*c* are hysteresis loop curves illustrating the effects produced by the improved heat treatment technique for a composition comprising $Mn_{1.2}Fe_{1.8}O_4$.

FIGURES 2*a*, 2*b* and 2*c* are hysteresis curves illustrating the effects produced by the improved heat treatment technique for the basic manganese ferrite composition with a chromium oxide additive and specifically

$$Mn_{1.225}Fe_{1.68}Cr_{.065}O_4$$

The degree of squareness of ferrite bodies as a criterion of their performance in memory systems applications may be evaluated as the induction ratio R_B. This ratio is found by first presenting a hysteresis loop at I_0 ampere turns (coercive force threshold) and measuring the change in induction B_{I_0}; then the current is increased so as to provide $1.6I_0$ ampere turns and the change in induction $B_{1.6I_0}$ is measured. The induction ratio R_B is

$$\frac{B_{1.6I_0}}{B_{I_0}}$$

and this ratio may be established for several different values of I_0 above the coercive threshold current. The maximum value of R_B that is obtained is considered a reliable indicator for high one to zero information ratios, which is a measure of performance of the ferrite body as a memory element.

The advantages obtained with the improved heat treatment techniques are demonstrated hereafter with respect to ferrites composed of manganese and iron oxides and with manganese ferrites to which a third oxide ingredient is added. The general formula for these ferrites is

$$Mn_{(3-a-b)}Fe_{(a)}M_{(b)}O_4$$

where M is Mg, Cu, Cr, Zn, Li, Al or Ni. It is to be understood, however, that the novel heating technique is not restricted to these manganese ferrite systems since the principles involved apply equally well to

$$Ni_{(x)}Fe_{(3-x)}O_4$$

and

$$Co_{(x)}Fe_{(3-x)}O_4$$

for example, and the chemical explanation applies similarly to these and other systems.

Usual ceramic techniques for forming a pressed "green" ferrite body comprise mixing commercially pure fine particle oxides in the desired proportions with intimate mixing obtained, for example, by wet ball milling to form a slurry. The slurry is thereafter dried and the dry cake subsequently ground to a fine powder. This powder is placed in an Alundum crucible and calcined in air at a temperature of about 1000° C. and again milled before the addition of a small amount of an organic binder and a lubricant material. The binder may conventionally be a polyvinyl alcohol added in an amount up to about 3% by weight of the calcined material and the lubricant may be magnesium stearate, for example, in an amount of about 0.5%.

The resulting plastic mixture is molded to a toroid or other desired shape at a pressure of about 10,000 to

20,000 pounds per square inch and in this condition is termed a "green" core. The binder that has been added makes the oxide particles cohere and the lubricant facilitates molding. Since both of these materials are organic compositions, they are driven off by heating in a subsequent process step.

Final thermal reaction and crystallization of the material usually is undertaken at temperatures of from 1200° C. to 1500° C. and it is within and following this step of the preparation that the present invention pertains. The novel technique comprises firing the green core to a temperature region where the spinel phase is stable and allowing the crystal grains to grow to a size from 3 to 30 microns depending on the coercivity desired in the final product. This temperature is hereafter referred to as the firing temperature. The next step is to cool the solid solution ferrite to a temperature zone where reoxidation and the formation of a new chemical phase such as α-Fe_2O_3 (hematite) or Mn_3O_4 can occur. This temperature is hereafter referred to as the annealing temperature. Both the cooling rate from the firing temperature to the annealing temperature and the time that the material is held at the lower temperature influence the grain size and occurrence of the α-Fe_2O_3 or other second phase crystalline form. At the high firing temperature the cations and anions of the mixed oxides diffuse and the spinel structure results. This formation is rapid and the length of time that heating is allowed to continue chiefly influences the rate of crystal growth.

The second phase composition or α-Fe_2O_3 that is produced during annealing after the desired grain size of the first phase is obtained, develops initially in the skin of the sample and the ferrite body is quenched from the annealing temperature when it is desired to stop growth of this latter phase. Alternatively, oxidation may be terminated by introducing an inert gas followed by slow cooling, which procedure is considered equivalent to quenching. It has been determined that holding the body at the annealing temperature for a prolonged period of time produces such a quantity and penetration of α-Fe_2O_3 that the improvement in hysteresis loop squareness and pulse performance is lessened and this step must be closely controlled.

The temperature at which the body is held during the annealing period is necessarily dependent upon the particular ferrite composition in question but may be considered as that range of temperatures in which the new phase or α-Fe_2O_3 can appear in the composition and is generally above 600° C. A number of different compositions are considered hereafter to demonstrate the temperatures determined for them and to indicate the generic application of the foregoing principle to ferrites generally.

The change in loop shape with firing procedure of a manganese ferrite $Mn_{1.2}Fe_{1.8}O_4$ is shown in FIGURES 1*a*, 1*b* and 1*c*. Appearance of α-Fe_2O_3 begins in this composition below 1050° C. and a sample annealed at this temperature (FIG. 1*b*) has the highest degree of squareness or the highest induction ratio R_B. The values of R_B for the manganese ferrite $Mn_{1.2}Fe_{1.8}O_4$ as obtained for several heating temperatures are given in the following table and correspond with the squareness of the hysteresis loop that may be observed graphically from FIGURE 1.

Table I

[Composition ($Mn_{1.2}Fe_{1.8}O_4$)]

Sample	Firing Temperature, ° C.	Time	Max. R_B
1	1,250	16.0 Hr.	2.1 (Fig. 1*a*).
2	1,250	16.0 Hr. (Then cooled to 1,050° C. 16 hr.).	4.0 (Fig. 1*b*).
3	1,250	16.0 Hr. (Cooled to 1,050° C.—16 hr., then 950° C.—3 hr.).	2.3 (Fig. 1*c*).

(All samples were quenched at end of the last temperature and time period indicated.)

The data given for sample 1 indicates that the aforementioned first chemical phase has been developed with little or none of the α-Fe_2O_3 crystalline form produced. Sample 2 illustrates the effect of annealing after the same firing temperature and time used for sample 1 and denotes the formation of a desired amount and penetration of the second phase material. Sample 3 illustrates the effect of a prolonged anneal even at a lower temperature after the same treatment as given to sample 2 and demonstrates the development of an excess amount of the second phase crystal form.

For this material, examination has corroborated the fact that the α-Fe_2O_3 persists in the skin of sample 2 without excessive penetration.

When selected ions M are added to the basic manganese ferrite as $Mn_{(3-a-b)}Fe_{(a)}M_{(b)}O_4$ and the special firing technique applied to ferrite bodies of this composition higher values of R_B are obtained. One typical example is with chromium as the additive in a sample $Mn_{1.255}Fe_{1.68}Cr_{.065}O_4$. Referring to FIGURES 2*a*, 2*b*, 2*c*, the loop shapes obtained with this composition are graphically illustrated, with the curve in FIGURE 2*a* representative of that obtained when the sample is fired at 1350° C. for 15 minutes and quenched, demonstrating substantially no formation of the second phase. FIGURE 2*b* indicates the result of the same treatment of another sample of the same composition but with subsequent cooling to 950° C. during which cooling interval the α-Fe_2O_3 phase is developed in the skin of the sample with increased squareness. FIGURE 2*c* demonstrates the effect of additional annealing at 950° C. with an amount of the α-Fe_2O_3 developed in this case in excess of the optimum and a reduced R_B ratio results.

A comparison of results other manganese ferrite compositions with additives is shown in the following tables which demonstrates attaining of an improved ratio R_B for the treatment procedure described. In addition, the one to zero signal ratio and switching times obtained with these samples is shown and may be observed to be superior when an optimum amount of α-Fe_2O_3 is allowed to develop in the skin of the sample as described. The switching speed is given in microseconds and is a measure of the interval of time required for the core sample to switch from one remanence state to the other. This is an important factor in connection with memory applications and it controls the operating cycle time of equipment in which such cores are incorporated. The marginal currents at which the one to zero ratios and switching speeds were measured are 670 ma./410 ma.

Table II

[Firing temperature 1,300° C. for 15 minutes, then quenched]

Composition	R_B	One to zero ratio	Switching Speed
$Mn_{1.255}Fe_{1.68}Cr_{.065}O_4$	3.6	2.5	2.0
$Mn_{1.21}Fe_{1.68}Mg_{.11}O_4$	4.0	3.5	1.9
$Mn_{1.08}Fe_{1.83}Cu_{.09}O_4$	3.6	3.0	2.0
$Mn_{1.14}Fe_{1.67}Mg_{.10}Cr_{.09}O_4$	3.3	2.5	1.9

Table III

[Firing temperature 1,300° C. for 15 minutes, cooled to 950° C., then quenched]

Composition	R_B	One to zero ratio	Switching Speed
$Mn_{1.255}Fe_{1.68}Cr_{.065}O_4$	5.5	3.8	1.5
$Mn_{1.21}Fe_{1.68}Mg_{.11}O_4$	5.2	4.9	1.58
$Mn_{1.08}Fe_{1.83}Cu_{.09}O_4$	5.0	4.0	1.45
$Mn_{1.14}Fe_{1.67}Mg_{.10}Cr_{.09}O_4$	3.8	3.2	1.3

Table IV

[Firing temperature 1,300° C. for 15 minutes, cooled to 950° C., refired to 950° C. for one hour, then quenched]

Composition	R_B	One to zero ratio	Switching Speed
$Mn_{1.255}Fe_{1.63}Cr_{.055}O_4$	3.8	3.0	1.9
$Mn_{1.21}Fe_{1.68}Mg_{.11}O_4$	4.0	3.5	1.8
$Mn_{1.08}Fe_{1.83}Cu_{.09}O_4$	3.9	3.0	2.0
$Mn_{1.14}Fe_{1.67}Mg_{.10}Cr_{.09}O_4$	3.0	2.5	1.8

The example given in the foregoing tables show that the method of controlled firing and annealing of ferrite bodies is desirable and produces optimal hysteresis characteristics for use in memory applications. Obviously every variation in annealing temperature and time for production of an ideal amount and penetration of the second chemical phase for each conceivable composition may not be presented but it is considered that the principle involved is adequately demonstrated by the examples given.

The composition of ferrites acted upon by the process of the present invention has been expressed in the tables in terms of atom numbers of constituents. It will be apparent to those skilled in the art that this composition may be readily converted to the more convenient representation of molecular percentages. When this is done, the corresponding molecular percentage constituents are the following:

	Mol percent
Fe_2O_3	about 38.7–43.5
MnO	about 51.6–58.4
Additives	about 0–8.8

While there have been shown and described and pointed out the fundamental novel features of the invention as applied to a preferred embodiment, it will be understood that various omissions and substitutions and changes in the form and details of the device illustrated and in its operation may be made by those skilled in the art without departing from the spirit of the invention. It is the intention therefore, to be limited only as indicated by the following claims.

What is claimed is:

1. A method of producing manganese ferrospinels for use as magnetic memory elements which bodies have a high degree of hysteresis loop squareness and are formed from compositions consisting essentially of about 38.7 to 43.5 mol percent Fe_2O_3, about 51.6 to 58.4 mol percent MnO and about 0–8.8 mol percent of at least one metallic oxide selected from the group consisting of chromium, magnesium, copper and nickel comprising mixing said oxide constituents, molding the mixture into a body, firing said body at a sintering temperature of about 1200°–1500° C. to form thereby a ferrospinel phase and thereafter reducing the temperature of said body in an oxidizing atmosphere to within the range of about 950°–1050° C. and holding for up to 16 hours to form an α-Fe_2O_3 phase in the skin region of said body rapidly and quenching said body to room temperature, preferably immediately from the lower of said latter temperature range to arrest further development of said α-Fe_2O_3 phase.

2. A method of producing manganese ferrospinels for use as magnetic memory elements which bodies have a high degree of hysteresis loop squareness and are formed from compositions consisting essentially of about 38.7 to 43.5 mol percent Fe_2O_3, about 51.6 to 58.4 mol percent MnO and about 0–8.8 mol percent of at least one metallic oxide selected from the group consisting of chromium, magnesium, copper and nickel comprising mixing said oxide constituents, molding the mixture into a body, firing said body at a sintering temperature of about 1200°–1500° C. to form thereby a ferrospinel phase and thereafter reducing the temperature of said body in an oxidizing atmosphere to about 950° C. wherein an α-Fe_2O_3 phase within the skin region of said body and rapidly quenching said body immediately to room temperature to arrest further development of said α-Fe_2O_3 phase.

3. A method of producing manganese ferrospinels for use as magnetic memory elements which such bodies have a high degree of hysteresis loop squareness and are formed from compositions consisting essentially of about 38.7 to 43.5 mol percent Fe_2O_3, about 51.6 to 58.4 mol percent MnO and about 0–8.8 mol percent of at least one metallic oxide selected from the group consisting of chromium, magnesium, copper and nickel comprising mixing said oxide constituents, molding the mixture into a body, firing said body at a sintering temperature of about 1200°–1500° C. to form thereby a ferrospinel phase and thereafter reducing the temperature of said body in an oxidizing atmosphere to about 1050° C. and holding at this temperature for up to 16 hours to form a second chemical phase α-Fe_2O_3 within the skin region of said body and rapidly quenching said body to room temperature to arrest further development of said α-Fe_2O_3 phase.

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