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MAGNETICALLY ANNEALED FERRITE MATERIAL

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This invention relates to magnetic ferrite material and, more particularly, to an improved method and means for magnetically annealing magnetic ferrite material.

The term "magnetic annealing" usually refers to a high-temperature treatment of material in a magnetic field which influences the magnetic properties of the material at ambient temperatures. For example, in materials susceptible to magnetic annealing, measurement of the hysteresis loop in the direction of the magnetic field applied while at high temperatures shows that a square loop has been produced. In other words, a preferred direction of magnetization has been effectively inserted into the material.

Material susceptible to magnetic annealing includes certain thin films, certain alloys, such as "Permalloy" and "Perminvar," and certain ferrites. As far as is known, only cobalt-containing ferrites have been described in the literature as being magnetically annealable. For example, see Smit and Wijn, in a book entitled "Ferrites," pages 310 through 317, published by Wiley in 1959. Also see United States Patent No. 2,929,787 to O. Eckert.

One of the most undesirable results occurring with the use of cobalt is that the coercive force of the ferrite material is raised. This requires more power to be used when this material is made into magnetic-memory cores, for example.

An object of this invention is to provide a method and means for magnetically annealing substantially cobalt-free ferrite material.

Another object of this invention is to provide a method and means for obtaining a magnetically annealed ferrite material which has a lower coercive force than magnetically annealed ferrite material containing cobalt.

Yet another object of the present invention is the provision of a novel method and means for magnetically annealing substantially cobalt-free nickel-ferrous ferrites and manganese-ferrous ferrites.

Still another object of this invention is the provision of magnetically annealed ferrite material which has its magnetic properties enhanced over the properties of previously known ferrite material.

These and other objects of this invention may be achieved by performing the sintering of the ferrite material desired to be magnetically annealed in an inert atmosphere. Thereafter, the ferrite material is given a special heat treatment which is believed to slightly oxidize the material, or to increase the oxygen content thereof by means of cation vacancies or other lattice defects. Thereafter, the ferrite material is heated to a temperature which may lie in the range between 200° C. and just below the Curie temperature of the material and is maintained at this temperature for a period of time such as one-half hour or more. A magnetic field is applied thereto while at this temperature. This field is maintained while the ferrite material is permitted to cool thereafter. The Curie temperature of the material is that temperature at which the material loses its magnetic properties.

The novel features that are considered characteristic of this invention are set forth with particularity in the appended claims. The invention itself, both as to its organization and method of operation, as well as additional objects and advantages thereof, will best be understood from the following description.

The initial steps used for preparing the ferrite materials in accordance with this invention do not differ from well-known procedures for preparing other ferrites. Mixing, calcining, regrinding, binder addition, granulation, and pressing are performed in the usual and well-known manner. However, in accordance with this invention, the firing or sintering of the material is carried out in any suitable inert atmosphere, such as nitrogen, argon, helium, or carbon dioxide. After sintering another heat treatment is applied to the material which, as best as can be presently determined, may produce a slight increase in the oxygen content of the ferrite by means of cation vacancies or other lattice defects and thus, although this second heat treatment may be carried out in an inert atmosphere, may constitute a slight oxidation.

A preferred method for accomplishing the subsequent heat treatment of the ferrite material can occur immediately after the ferrite material has been maintained at its sintering temperature for the desired length of time. The sintering temperature may vary from approximately 1200° C. to 1450° C., depending upon the composition of the material. After such sintering in an inert atmosphere, which lasts from one to several hours, the magnetic material is slowly cooled while still in the inert atmosphere to a temperature which may be on the order of and within the range from 200 to 500° C. below the sintering temperature. Such cooling occurs at a rate which is slow when compared to the rate at which cores are cooled when quenched by being placed in ambient temperature. This slow rate of cooling can be on the order of 200° per hour. Such cooling occurs while the ferrite material is still in the inert atmosphere. As soon as the lowered temperature is reached, the ferrite material is then quenched by being placed in the ambient temperature or permitted to cool rapidly to room temperature, while still in the protective atmosphere.

Thereafter, the magnetic annealing step is performed. The requirements of this treatment are not critical, providing the threshold values of time, temperature, and magnetic field are exceeded. A typical treatment is to reheat the ferrite material which has received the just-described treatment to a temperature which may lie within the range of from 200° C. to a temperature below the Curie temperature of the material, for a time such as 15 minutes, but this heat treatment can also be applied up to several hours. While the material is maintained at this temperature, a magnetic field on the order of several oersteds is applied to the material. The direction of the field determines the orientation of the preferred direction of magnetization.

Thus, using by way of example magnetic cores, which are simple toroids, one way for achieving the desired orientation is to thread the cores on a wire through which current is applied to achieve the desired field orientation in the toroid ring of the magnetic-cores material. Alternatively, the ferrite material may be surrounded by a solenoid for applying the field to the material which is positioned therein to achieve a desired direction of orientation. Also, the required field may be obtained by placing the material to be treated between the poles of a permanent magnet. The ferrite material being magnetically annealed may have any desired shape and is not to be considered to be restricted to toroidal-core shapes, although this description is made in connection with toroidal cores. Multiaperture magnetic-ferrite cores, which have a central or main aperture and smaller apertures in the toroidal ring, may have such magnetic field applied thereto, ether by threading the current-carrying wire through the central main aperture or by threading the current-carrying wire through one of the smaller apertures, whereby the material around the threaded aperture will have substantially square-loop hysteresis characteristics while the material in the remainder of these multiaperture cores will have a "linear" material therein. Although not necessary, it is preferred to allow the material to cool while the magnetic field is applied thereto.

The quench of the material, which has been slowly cooled below the sintering temperature, need not occur immediately upon reaching the temperature below the sintering temperature. Material may be left at this temperature for some time before the quenching occurs. The preferred rate of cooling may be achieved by leaving the magnetic cores which have been sintered in the oven, but turning off the current which is used for heating the oven.

Still another method for the desired intermediate temperature treatment for the ferrite material may be practiced by quickly quenching the ferrite material in a protective atmosphere on the completion of the sintering treatment. Thereafter, the ferrite material may be reheated in an inert atmosphere also to a temperature of from 200° to 500° below the sintering temperature. The material may then be quenched by being placed in the ambient temperature while still in a protective atmosphere. Magnetic annealing is thereafter applied in the same manner as has been previously described.

Still another method of intermediate temperature treatment can be to take the ferrite material, which has been sintered in the inert atmosphere and thereafter quenched in the inert atmosphere, and to reheat it in air at a lower temperature (approximately 500° C. to 900° C.), for a shorter time than in the inert atmosphere, on the order of fifteen minutes. The ferrite material can then be cooled and thereafter magnetically annealed in the manner previously described.

These alternative "intermediate heat treatments" which require a reheating of the material, although effective to enable magnetic annealing of the material, are not preferred, since it is much simpler to allow the material to slowly cool just after sintering and then to quench from the indicated temperature than to reheat.

It has been stated that the intermediate-temperature treatment produces a slight increase in the oxygen content of the ferrite. It should be understood that this is the best-known explanation of the phenomenon which occurs at this time. It has been noted that magnetic-ferrite material which is rapidly cooled from the sintering temperature cannot be magnetically annealed. However, when this same material is treated in accordance with this invention, it can be magnetically annealed.

The range of compositions which has been found to respond to magnetic annealing is slightly different for manganese than for nickel. For manganese-ferrous ferrites, the range of compositions, in mol percent, includes

$$0.87MnFe_2O_4 \cdot 0.13Fe_3O_4$$

to $0.60MnFe_2O_4 \cdot 0.40Fe_3O_4$. For nickel-ferrous ferrites the corresponding range of compositions, in mol percent, extends from $0.80NiFe_2O_4 \cdot 0.20Fe_3O_4$ to

$$0.50NiFe_2O_4 \cdot 0.50Fe_3O_4$$

Small percentages of a third component, such as $ZnFe_2O_4$, $MgFe_2O_4$, $CuFe_2O_4$, and $CoFe_2O_4$, have also been included in some of the compositions within the ranges given. Of these, the $ZnFe_2O_4$ and $MnFe_2O_4$ up to 20 percent seem to be rather neutral. $CuFe_2O_4$ harms the squareness; $CoFe_2O_4$ raises the coercive force. In ferrite materials which include cobalt oxide, in order to enable magnetic annealing, percentages on the order of .05 percent or .1 percent of cobalt creates sensitivity to magnetic annealing. In the present invention, in all the chemicals used, namely, iron oxide, nickel oxide, and manganese carbonate, an analysis indicates cobalt contents of less than 0.01 percent. Therefore, when the term "substantially cobalt-free ferrites" is employed herein, it is intended to mean that there is less than 0.01 percent of cobalt present therein.

By way of illustration of a specific example of a nickel-ferrous ferrite which was prepared in accordance with this invention, the composition of the material in mol percent comprised $0.60 NiFe_2O_4 \cdot 0.40Fe_3O_4$. The material was pressed to have the form of toroidal cores. The sintering temperature was on the order of 1285° C., which was maintained at one hour. The inert atmosphere in which these cores were sintered was nitrogen. The cores were then permitted to slowly cool in the inert atmosphere to a temperature of 1025° C. over the period of one hour. After holding the temperature at 1025° C. for fifteen minutes, the ferrite cores were permitted to be quenched to the ambient temperature (around 25° C.) while the nitrogen atmosphere was maintained.

For the magnetic annealing step, the cores were strung on a wire which was inserted in the oven, into which external electrical connections were made. The temperature of the cores was then raised up to 260° C., which was maintained for one hour. During this time and thereafter while the cores were permitted to cool down to room temperature, electrical current was applied to the wire on the order of 5.4 amperes, thus establishing a magnetic field on the order of 12.5 oersteds. The properties of cores prepared in accordance with this method are shown in Table I below: (The core size was 80 mils O.D., 50 mils I.D., and 25 mils high.)

TABLE I

Pulse Properties of Nickel-Ferrous Ferrite, Magnetically Annealed

Temp. (° C.)	Drive[1] (ma.)	Output (mv.)	Noise (mv.)	t_p(μs.)	t_s(μs.)	knee (ma.)	Disturb Ratio
−60	1500/750	150	24	0.65	1.26	1,180	0.79
+25	1500/750	195	24	.58	1.14	1,090	.73
+60	1500/750	200	28	.50	1.10	1,050	.70
+100	1500/750	280	31	.43	0.96	960	.65

[1] t_r=0.2μs.; t_d=5μs.; disturb repeated 20 times.

Table I gives the results of the coincident current pulse test as the function of temperature for a magnetically annealed toroidal core of the nickel-ferrous ferrite composition given above. Two important improvements over conventional square-loop ferrite cores can be seen immediately from this table. First, a change over a range of 150° C. centering around room temperature gives a total change in "knee" of only 20 percent. Magnesium-manganese square-loop ferrites operating in the same range show a change in the knee of approximately 300 percent. Another property is that the cores tested show an unusually high ratio of knee to drive (equals disturb ratio). Magnesium-manganese ferrite cores, which are considered good, exhibit over the same temperature range a disturb ratio approximately fifteen percent lower than that for these magnetically annealed cores. This means that the effects of disturb pulses on cores made in accordance with this invention are better than the best of other types of cores. The ratio 1500/750, shown under "drive," indicates the ratio of the drive-current pulse in milliamperes to the half-drive current pulse in milliamperes. The noise millivolts were measured by determining the voltage obtained when a disturb pulse on the order of 750 millivolts was employed. t_p represents the peaking time, or time required from the commencement of drive to obtain a maximum output; t_s represents the total switching time required to drive a core. The knee has been generally defined as that applied current which begins to switch the core, rather than give a reversible "noise voltage." The disturb ratio is the ratio of this same current to the current used to switch the core.

Another example of a nickel-ferrous ferrite composition in mol percent which was made up into cores is $0.80NiFe_2O_4 \cdot 0.20Fe_3O_4$. This composition was fired at 1330° C. for over an hour. It was then slowly cooled to 1060° C. by being left in the oven with the heat turned off. From this temperature it was quenched by being placed in the ambient temperature (about 25° C.). During the firing, slow cooling, and quenching operation, the cores were still maintained in the nitrogen atmosphere. After quenching to the ambient temperature, these cores were magnetically annealed by raising them to a temperature of 260° C. and maintaining this temperature for at least one hour while applying a magnetic field of 12 oersteds thereto. The material was then permitted to cool. It exhibited the improved characteristics of the type indicated in Table I.

Another example of a composition in mol percent which could be magnetically annealed only after the heat treatment of the type indicated was one employing $0.70NiFe_2O_4 \cdot 0.30Fe_3O_4$. After the usual mixing, calcining, grinding, and pressing into cores, the cores were sintered at a temperature of 1320° C. for at least one hour. The composition was then slowly cooled to 1060° C. The material was then quenched by being exposed to the ambient temperature (about 25° C.). An inert atmosphere was maintained throughout these procedures. Thereafter, the material was magnetically annealed by heating to 260° C. and maintaining this temperature for an hour while applying a magnetic field of 12 oersteds thereto.

Still another composition in mol percent which responded to magnetic annealing and provided superior results of the type indicated was one employing

$$0.50NiFe_2O_4 \cdot 0.50Fe_3O_4$$

This composition was fired at 1300° C. in an inert atmosphere of nitrogen. It was then slowly cooled to 1040° C. while the inert atmosphere was maintained. Thereafter, it was quenched by being placed in the ambient temperature (about 25° C.), while an inert atmosphere was maintained thereon. It was magnetically annealed by heating the material to 260° C., maintaining this for an hour. A magnetic field on the order of 12 oersteds was also applied.

Yet another example of a substantially cobalt-free ferrite which was magnetically annealed comprises, in mol percent, $0.5NiFe_2O_4 \cdot 0.1MnFe_2O_4 \cdot 0.4Fe_3O_4$. The firing temperature was 1320° C. and an inert atmosphere was provided. The material was slowly cooled to 1025° C. and then quenched by being placed in the ambient temperature, but the inert atmosphere was maintained. The material was then magnetically annealed by being reheated to 400° C. for five minutes in a magnetic field of 3.6 oersteds. This example illustrates that the method of magnetically annealing in accordance with this invention will apply to mixtures of nickel and manganese ferrites. Furthermore, by raising the temperature during the magnetic annealing, the field strength and application time can be reduced. This is not a preferred treatment, however, but the treated specimen does exhibit magnetic-annealing characteristics.

Another batch of material having the composition $0.6NiFe_2O_4 \cdot 0.4Fe_3O_4$ was mixed and sintered at 1300° C. in an inert atmosphere. It was then quickly quenched to the ambient temperature while still in an inert atmosphere. It was thereafter reheated to 800° C. for one-half hour while in an inert atmosphere. It was then quenched while in the inert atmosphere. It was then magnetically annealed by being reheated to 250° C. for three-fourths of an hour in a magnetic field of 10 oersteds.

Table II below shows the properties of magnetically annealed ferrite cores having the composition in mol percent of $0.75MnFe_2O_4 \cdot 0.25Fe_3O_4$. This material was fired for two hours in an inert atmosphere of nitrogen at a temperature of 1270° C. It was thereafter slowly cooled to 1025° C. and quenched by being placed in the ambient temperature (about 25° C.). The inert atmosphere was maintained during the second heat treatment and the ambient quench. A magnetic-annealing procedure was then applied by then reheating the material to 200° C. and maintaining the temperature for one hour, while applying a field of 16 oersteds. The material was then permitted to cool down to room temperature with the field applied. The core size was 80 mils O.D., 50 mils I.D., and 25 mils high.

TABLE II

Pulse Properties of Manganese-Ferrous Ferrite, Magnetically Annealed

Temp. (° C.)	Coercive Force (ma.)	B_r/B_s Ratio
−30	220	0.90
0	250	.92
+30	280	.93
+100	290	.95

It will be seen from Table II that the magnetically annealed manganese-ferous ferrite maintains its magnetic properties over a temperature range of from −30° C. to +100° C. The disturb ratio of these cores is approximately 0.5 percent. The hysteresis characteristics are represented by the B_r/B_S ratio. The major-loop data is given instead of the minor-loop data, since manganese-ferrous-ferrite cores are suitable for linear selection systems, but are not sufficiently rectangular for coincident current use. However, the coercive force property for the cores as shown in Table II is about one-fourth of that of nickel-ferrous ferrites and is substantially as low as that of any of the usually employed square-loop ferrite materials. The region of approximately constant coercive force (and therefore indicative of the required drive) is maintained constant at higher temperatures than that of nickel-ferrous ferrites.

Another batch of ferrite material having the same heat treatment was magnetically annealed by being heated to a temperature of 250° C. for one hour. The field applied, however, was only 3.5 oersteds. The higher temperature apparently reduces the required magnetic field strength for annealing.

Another example of a manganese-ferrous-ferrite composition which, in accordance with this invention, was magnetically annealed and which displayed similar superior properties, as indicated in Table II, was a composition in mol percent of $0.60MnFe_2O_4 \cdot 0.40FeO_4$. This was sintered at a temperature of 1300° C. for at least one hour. The material was then cooled slowly to 1040° C. It was thereafter quenched in the ambient temperature (about 25° C.). An inert atmosphere of carbon dioxide was maintained during all this treatment. The magnetic-annealing step required the raising of the materials to a temperature on the order of 275° C. and maintaining this temperature for at least one-half an hour while applying the magnetic field of 25 oersteds. The material, as indicated, had superior coefficient properties as well as a low coercive force on the order of that indicated in Table II.

Still another illustration of the composition, in mol percent, of cores demonstrating superior properties as exemplified in Table II was one wherein

$$0.80MnFe_2O_4 \cdot 0.20Fe_3O_4$$

was employed. This material was also fired to 1300° C., then slowly cooled to 1060° C. and quenched. All this procedure was done in an inert atmosphere which employed nitrogen. The material was raised to a temperature between 200° and 300° and maintained at that temperature for one-half hour, while a field of 9 oersteds was applied. The material then was cooled with the field applied.

Yet another magnetic-ferrite material which was magnetically annealed in accordance with this invention to provide the superior properties of the type indicated was a composition, in mol percent, of

$$0.70MnFe_2O_4 \cdot 0.30Fe_3O_4$$

This material was sintered at 1160° C. and then cooled to 700° C. It was then quenched in the ambient temperature. An inert atmosphere was maintained during all this procedure. This material was then magnetically annealed by being raised to a temperature of 260° C. for at least twenty minutes, while a field of 14 oersteds was applied thereto.

One other example of substantially cobalt-free ferrite material which was magnetically annealed was a composition, in mol percent, of $0.87MnFe_2O_4 \cdot 0.13Fe_3O_4$. This was sintered in an inert atmosphere at 1230° C. and then quenched to ambient temperature while in an inert atmosphere. The material was then reheated while in an inert atmosphere to 800° C. for two and one-half hours. It was then quenched. The magnetic annealing was carried out at a temperature of 260° C. for one-half hour with a magnetic field of 12 oersteds being applied.

There has accordingly been described and shown here in a method and means of magnetically annealing ferrite material which is substantially cobalt free whereby material having a low temperature coefficient, a high disturb ratio, and a preferred direction of magnetization is produced. It has ben found that when cores made in accordance with the method of this invention are fabricated into a magnetic-core memory, the memory can be operated without current or temperature compensation over a range of temperatures between −55° and 100° C.

I claim:

1. The method of magnetically annealing substantially cobalt-free manganese-ferrous-ferrite material having a composition in mol percent selected from the range from $0.87MnFe_2O_4 \cdot 0.13Fe_3O_4$ to $0.60MnFe_2O_4 \cdot 0.40Fe_3O_4$, said method comprising sintering said material at a temperature between 1150° C. and 1450° C. while in an inert atmosphere, quenching said material while in an inert atmosphere, heating said material to a temperature between 200 to 500 degrees centigrade below said sintering temperature while in an inert atmosphere, quenching said material while in an inert atmosphere, heating said material to a temperature between 200 degrees centigrade and the Curie temperature, maintaining said material at said temperature for at least 15 minutes, applying a magnetic field to said material while said temperature is maintained, and allowing said material to cool while said magnetic field is applied.

2. The method of magnetically annealing substantially cobalt-free nickel-ferrous-ferrite material having a composition in mol percent in the range from $0.80NiFe_2O_4 \cdot 0.20Fe_3O_4$ to $0.50NiFe_2O_4 \cdot 0.50Fe_3O_4$, said method comprising sintering said material at a temperature between 1150° C. and 1450° C. while in an inert atmosphere, quenching said material while in an inert atmosphere, heating said material to a temperature between 200 to 500 degrees centigrade below said sintering temperature while in an inert atmosphere, quenching said material while in an inert atmosphere, heating said material to a temperature between 200 degrees centigrade and the Curie temperature, maintaining said material at said temperature for at least 15 minutes, applying a magnetic field to said material while said temperature is maintained, and allowing said material to cool while said magnetic field is applied.

3. The method of magnetically annealing substantially cobalt-free manganese-ferrous-ferrite material having a composition in mol percent selected from the range from

$$0.87MnFe_2O_4 \cdot 0.13Fe_3O_4 \text{ to } 0.60MnFe_2O_4 \cdot 0.40Fe_3O_4$$

said method comprising sintering said material at one of the temperatures between 1150° C. and 1450° C. in an inert atmosphere, allowing said material to cool to a temperature at least 200 to 500 degrees centigrade below sintering temperature at a rate which is slow when compared to an ambient quench rate while in said inert atmosphere, quenching said material while in said inert atmosphere, heating said quenched material at a temperature between 200 degrees centigrade and the Curie temperature, maintaining said material at said temperature for at least 15 minutes, applying a magnetic field to said material while heated, and allowing said material to cool while said magnetic field is applied.

4. The method of magnetically annealing substantially cobalt-free nickel-ferrous-ferrite material having a composition in mol percent in the range from

$$0.80NiFe_2O_4 \cdot 0.20Fe_3O_4 \text{ to } 0.50NiFe_2O_4 \cdot 0.50Fe_3O_4$$

said method comprising sintering said material at one of the temperatures between 1150° C. and 1450° C. in an inert atmosphere, allowing said material to cool to a temperature at least 200 to 500 degrees centigrade below sintering temperature at a rate which is slow when compared to an ambient quench rate while in said inert atmosphere, quenching said material while in said inert atmosphere, heating said quenched material at a temperature between 200 degrees centigrade and the Curie temperature, maintaining said material at said temperature for at least 15 minutes, applying a magnetic field to said material while heated, and allowing said material to cool while said magnetic field is applied.

5. The method of magnetically annealing substantially cobalt-free manganese-ferrous-ferrite material having a composition in mol percent selected from the range from

$$0.87MnFe_2O_4 \cdot 0.13Fe_3O_4 \text{ to } 0.60MnFe_2O_4 \cdot 0.40Fe_3O_4$$

said method comprising sintering said material at a temperature between 1150° C. and 1450° C. while in an inert atmosphere, cooling said material to the ambient temperature while in an inert atmosphere, heating said material to a temperature in the range between 500 to 900 degrees centigrade, cooling said material, reheating said material to a temperature in the range between 200 degrees centigrade and the Curie temperature, maintaining said material at said last-named temperature for at least 15 minutes, applying a magnetic field to said material while said temperature is maintained, and allowing said material to cool while said magnetic field is applied.

6. The method of magnetically annealing substantially cobalt-free nickel-ferrous-ferrite material having a composition in mol percent in the range from

$$0.80NiFe_2O_4 \cdot 0.20Fe_3O_4 \text{ to } 0.50NiFe_2O_4 \cdot 0.50Fe_3O_4$$

said method comprising sintering said material at a temperature between 1150° C. and 1450° C. while in an inert atmosphere, cooling said material to the ambient temperature while in an inert atmosphere, heating said material to a temperature in the range between 500 to 900 degrees centigrade, cooling said material, reheating said material to a temperature in the range between 200 degrees centigrade and the Curie temperature, maintaining said material at said last-named temperature for at least 15 minutes, applying a magnetic field to said material while said temperature is maintained, and allowing said material to cool while said magnetic field is applied.

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