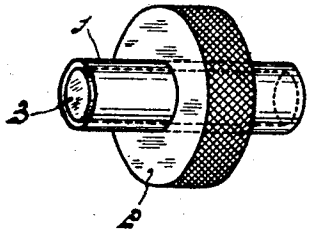
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SOFT FERROMAGNETIC MATERIAL AND METHOD OF MAKING SAME

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SOFT FERROMAGNETIC MATERIAL AND METHOD OF MAKING SAME

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This invention relates to inductance coils for high frequencies, inter alia frequencies exceeding 1000 kc./s. and more, particularly for radio purposes, comprising a magnetic core containing cubic ferrite as a magnetic material, and further relates to such cores.

From French Patent Specification 887,083 it is known to provide a sufficiently high content of oxygen in the preparation of ferrites. It is thus possible to obtain ferrites which are very suitable for use in inductance coils employed for frequencies up to 1000 kc./s. and giving rise in this case to very low losses only. For this frequency range a loss factor $tg\delta$ lower than 6% may be attained. However, if the ferrites as described should be used for coils with which higher frequencies occur, for example coils for oscillatory circuits for radio purposes or for high-frequency transformers. The magnetic losses appear to increase considerably at these frequencies.

Magnetic cores containing cubic homogeneous mixed crystal ferrites as a magnetic material have also been described in U. S. Patents 2,452,529, 2,452,530, and 2,452,531, issued October 26, 1948. These patents generally described mixed crystal ferrites having large magnetic permeabilities and low magnetic losses.

The invention makes it possible, with the use of such a ferrite, to manufacture a coil which also exhibits very favourable properties with respect to losses for frequencies exceeding 1000 kc./s.

According to the invention, the magnetic material used is a cubic ferrite thoroughly reacted having a specific electric resistance of at least 100 ohms/cm., a Curie-point of at least 75° C. and an initial permeability comprised between 20 and 150.

To make the invention better understood, it may be observed that it is based on the determination that a high initial permeability of the sintered core of ferrite is attended with high losses at frequencies exceeding 1000 kc./s., even if the oxygen content is high. It is remarkable that, whereas the aim will usually be to attain high permeability, it is found to be advantageous, according to the invention, to restrict the permeability to lower values. In this connection it may be remarked that a permeability of from 20 to 150 is appreciably higher than permeability of powdered iron cores intended for use at high frequencies (higher than 1000 kc./s.), this permeability being about 10.

It was hitherto not known that the value of the initial permeability directly affects the value of the magnetic losses, although French Patent

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Specification 887,083 already disclosed that the obtainment of high permeabilities and low losses might to a certain extent conflict with one another. However, this is due to secondary phenomena, that is to say due to the fact that measures which are favourable for obtaining high permeability, such as a high sintering temperature to ensure homogeneous ferrite, are disadvantageous for the obtainment of an adequate content of oxygen. By ensuring a high degree of homogeneity by other means, for example by using particularly reactive compounds in the preparation of ferrite, these difficulties may be obviated and high permeabilities can be combined with low losses, at least for frequencies below 1000 kc./s.

It has now been found, however, that the value of the permeability is intimately connected with that of the losses and that, for frequencies exceeding 1000 kc./s., it is advantageous to restrict the permeability to low values.

A measure is probably constituted by the value of the product $\lambda 6$ and the value of the crystal anisotropy, which reacts on the permeability in the same sense as $\lambda 6$, but which usually has a smaller influence. As is well-known, the initial permeability of magnetic material, when the crystal anisotropy is neglected, is expressed by a formula of the form

$$\mu_0 = \frac{I^2_{max}}{\lambda 6}$$

in which I_{max} represents the saturation magnetisation, λ the magneto-striction and 6 the mean value of the strains in the material (vide Becker and Döring: Ferromagnetismus, 1939, page 155). A high value of $\lambda 6$ would, in this case, be conductive to obtaining low losses at high frequencies higher than 1000 kc./s. A high value of $\lambda 6$ implies a low value of μ.

In order that, at a high value of $\lambda 6$, the initial permeability may have a maximum value, it is advantageous to have a high saturation magnetisation. According to the invention, this is ensured by using ferrites having a Curie-point of at least 75° C., preferably a Curie-point of at least 250° C. This is, moreover, advantageous since the magneto-striction and the crystal anisotropy of ferrite increase as the distance from the Curie-point increases. Thus, a high Curie-point is conducive to low losses at high frequencies. The term "Curie-point" is, in this case, to be understood to mean the temperature at which the initial permeability has decreased to 10% of the maximum value, in other words, the temperature at which magnetic material passes into a

state which is to be regarded as non-magnetic for practical purposes.

In order to ensure a high value of 6 or at least low initial permeability combined with the desired low high-frequency losses, a particular embodiment of the invention utilises ferrite of a composition comprising less than 50 mol. percent of iron-oxide.

In order to ensure low losses it is furthermore necessary that a ferrite according to the invention should be reacted as completely as possible, that is to say that the metal compounds used in the preparation of ferrite should be completely converted into homogeneous ferrite, although thorough reaction in itself is conducive to high permeability.

The degree of homogeneity may be judged from the variation of the initial permeability with temperature at the Curie-point, since ferrite which has been reacted insufficiently exhibits a less important decline in permeability at the Curie-point than ferrite which has been reacted completely. The greatest possible reaction may be ensured either by using as an initial material a very finely-divided mixture, or by sintering the mixture repeatedly, in which event the sintered mixture is required to be pulverised prior to the next sintering process. The two steps may also be taken in combination. The last sintering process is to be effected at a higher temperature than the preceding one, in order to ensure adequate compactness. Each sintering process is preferably effected at a higher temperature than its preceding one.

In this case care should be taken to ensure that the highest sintering temperature does not become so high that the ferrite would split off oxygen and is not capable of absorbing a sufficient quantity of oxygen during the subsequent cooling process. The oxygen content is required to be at any rate such that the specific resistance is at least 100 ohms/cm., in order to ensure that eddy-current losses are so small as to be negligible. The sintering treatment is preferably effected at a temperature below 1300° C.

In order to ensure thorough reaction of the ferrite at low sintering temperature within a reasonable time, it is advisable in the preparation of ferrite to utilise as an initial material a ferrite-forming mixture containing active iron-oxide. A thoroughly reacted product may thus be obtained even at sintering temperatures below 1100° C. Thus, for example, the starting material may be a mixture which is obtained by causing the metal constituents of ferrite to be deposited in common from a solution. Such a mixture may already partly exhibit ferrite structure.

According to the invention, an inductance coil having very favourable high-frequency properties may be obtained if use is made of a core comprising nickel-zinc ferrite as a magnetic material. The term "nickel-zinc-ferrite" is to be understood to mean a ferrite which is substantially constituted by nickel oxide, zinc oxide and iron oxide. A nickel-zinc-ferrite having the desired properties is obtained by providing that a very finely-divided mixture consisting of nickel, zinc and iron compounds having a size of grain smalled than 1μ, preferably a mixture of oxides containing active iron oxide, is heated in an atmosphere containing oxygen and by subsequent cooling, if necessary stepwise, in such an atmosphere.

The mixing ratio between the ferrite-forming constituents is preferably chosen to be such that

the ferrite contains at least 10 mol. per cent of nickel oxide, at least 10 mol. per cent of zinc oxide and from 40 to 60 mol. per cent of iron oxide. Very low losses may be obtained when using a composition of 34–36 mol. per cent of nickel oxide, 15–18 mol. per cent of zinc oxide and 48–50 mol. per cent of iron oxide.

The use of nickel-zinc-ferrite according to the invention permits of obtaining values for

$$\frac{tg\delta}{\mu_0}$$

which are lower than 1.10^{-3} at 10 mc./s. In this case

$$tg\delta \text{ equals } \frac{R}{\omega L}$$

in which R is the loss resistance, measured whilst avoiding dielectric and ohmic losses, L is the inductance of a coil wound on an annular core; and ω is the circle frequency.

In a further embodiment of the invention a manganese-zinc-ferrite is used in an inductance coil. The term "manganese-zinc-ferrite" is to be understood to mean ferrite which is substantially composed of manganese oxide, zinc oxide and iron oxide. This ferrite preferably contains at least 10 mol. per cent of manganese oxide, at least 10 mol. per cent of zinc oxide and from 40 to 60 mol. per cent of iron oxide.

The preparation of manganese-zinc-ferrite according to the invention is required to be effected with great care, since it has been found that in the case of such a ferrite very accurate dosing of the oxygen content is essential and that, in case of over-dosage, ferrite of inferior quality ensues. This is probably due to the fact that manganese may exhibit different valency stages and is liable to pass to a higher valency stage whilst absorbing oxygen, the magnetic properties thus being detrimentally affected. In view thereof it is of importance to carry out the sintering process of the ferrite at such temperature and to perform the sintering and cooling processes in an atmosphere of such oxygen partial pressure that minimum oxidation of manganese occurs.

Correct dosing of oxygen may be obtained by cooling the ferrite, subsequent to sintering, in an atmosphere the oxygen partial pressure of which decreases in accordance with the decrease in temperature. Thus, for example, an indifferent gas mixed with oxygen obtained by electrolysis of an aqueous solution may be caused to flow along the ferrite and the oxygen content may be reduced, as the temperature of the ferrite decreases, by reducing the electrolysing current. The most suitable oxygen content can be readily determined experimentally.

As an alternative, the ferrite may be subjected to a stream of gaseous oxygen compound which splits off oxygen at increased temperature, to an extent which is smaller as the temperature decreases. Very satisfactory results are obtained, for example, by conducting overheated water vapour along the ferrite, the vapour being mixed, if necessary, with an indifferent gas such as nitrogen. At the sintering temperature of the ferrite the water vapour is splitted partly into hydrogen and oxygen and the oxygen partial pressure gradually decreases upon decrease in temperature. The sole figure of the accompanying drawing diagrammatically shows an inductance coil according to the invention. In this figure reference numeral 1 designates a coil frame of insulating material, 2 the winding of the coil and 3 a rod-shaped magnetic core.

Examples

1. A deposit is produced from a solution of nickel sulphate, zinc sulphate and iron nitrate by means of a solution of soda, the deposit being dried and subsequently heated for 1 hour in air at 900° C. The powder thus obtained, containing 22.5 mol. per cent of nickel oxide (NiO), 31.3 mol. per cent of zinc oxide (ZnO) and 46.2 mol. per cent of iron oxide (Fe_2O_3) is moulded to form a ring by using a pressure of 3 tons/cm.^{2}. This ring is heated for 1 hour at 1000° C. in oxygen and subsequently slowly cooled in oxygen, at the rate of about 5° a minute. The table shows the properties of the core obtained.

2. In the manner as described in Example 1, a powder is prepared of the composition 34.6 mol. per cent of NiO, 17.2 mol. per cent of ZnO, and 48.2 mol. per cent of Fe_2O_3 and moulded to form a ring, followed by sintering for 1 hour at 1300° C. in oxygen and subsequently show cooling in oxygen. The results obtained are mentioned in the table.

3. A mixture consisting of 24.8 mol. per cent of NiO, 31.2 mol. per cent of ZnO, and 44.0 mol. per cent of Fe_2O_3, obtained by grinding these oxides in a ball mill for four hours, is heated for 1 hour at 800° C. in air, then ground again and subsequently moulded to form a ring. This ring is heated for 1 hour at 1050° C. in oxygen, followed by slow cooling. The results obtained are mentioned in the table.

4. A mixture consisting of 23.4 mol. per cent of MnO_2, 26.2 mol. per cent of ZnO and 50.4 mol. per cent of Fe_2O_3 is ground for a week, moulded into a ring and then heated for 5 hours at 1000° C. in a stream of overheated water vapour. Subsequently, cooling takes place to 300° C. in the furnace, during which process the stream of water vapour continues. The properties of the core obtained are shown in the table.

Table

	Example 1	Example 2	Example 3	Example 4
μ_0	50	85	65	55
Curie-point ° C	250	465	250	100
Spec. weight	4.2	5.0	4.4	3.1
10^2 tg δ at 2 mc./sec.	1.1	1.3	1.1	1.4
5	1.3	1.3	1.6	2.2
10	1.7	1.3	4.6	6.0
20	3.1	2.0	21.0	26.0
$10^4 \frac{tg\ \delta}{\mu}$ at 2 mc./sec.	2.2	1.5	1.7	2.5
5	2.6	1.5	2.5	4.0
10	3.4	1.5	7.0	19.0
20	6.2	2.4	32	47

For the purpose of defining the terms "ferrite," "mixed crystal," and "soft" magnetic materials, the following definitions will be employed in connection with the above-noted terms as used throughout the specification and in the appended claims.

A "ferrite" is a crystalline material which is a compound of the reaction product of a metal oxide and iron oxide having the empirical formula MFe_2O_4 wherein M represents a bivalent metal. This material may also be defined as a metallic salt of the hypothetical acid $H_2Fe_2O_4$.

A "mixed crystal" ferrite is a ferrite material comprising two or more ferrites as hereinbefore defined which are chemically combined together to form a single homogeneous crystalline compound.

The term "soft" magnetic material means magnetic material having a low remanence and a low coercivity when the applied inductive field is removed from the material.

Within the scope of the definitions noted above, we have described our invention with specific examples and methods of execution, which, however, will suggest other obvious modifications to those skilled in the art without departing from the spirit and scope of our invention.

What we claim is:

1. A soft ferromagnetic material having low magnetic losses up to about 20 mc./sec. and which is particularly adapted for use in cores in inductance coils and the like employed in circuits operating at frequencies up to 20 mc./sec., consisting essentially of substantially homogeneous mixed crystals of nickel-zinc ferrite having an initial magnetic permeability of about 20 to 150 and consisting of the heat reaction product of about 10 to 35 mol. per cent of NiO, about 40 to 60 mol. per cent of Fe_2O_3, and the remainder ZnO in an amount at which the Curie point of the nickel-zinc ferrite exceeds 250° C. and comprises at least 10 mol. per cent.

2. A soft ferromagnetic material having low magnetic losses up to about 20 mc./sec. and which is particularly adapted for use in cores in inductance coils and the like employed in circuits operating at frequencies up to about 20 mc./sec., consisting essentially of substantially homogeneous mixed crystals of nickel-zinc ferrite having an initial magnetic permeability of about 20 to 150 and consisting of the heat reaction product of about 10 to 35 mol. per cent of NiO, about 40 to 60 mol. per cent of Fe_2O_3 and about 10 to 31 mol. per cent of ZnO, said ZnO comprising an amount at which the Curie point of the nickel-zinc ferrite exceeds 250° C.

3. A soft ferromagnetic material having low magnetic losses up to about 20 mc./sec. and which is particularly adapted for use in cores in inductance coils and the like employed in circuits operating at frequencies up to about 20 mc./sec., consisting essentially of substantially homogeneous mixed crystals of nickel-zinc ferrite having an initial magnetic permeability of about 20 to 150 and consisting of the heat reaction product of about 34 to 36 mol. per cent of NiO, 15 to 18 mol. per cent of ZnO, and 48 to 50 mol. per cent of Fe_2O_3, said nickel-zinc ferrite having a Curie point of at least 250° C.

4. A soft ferromagnetic material having low magnetic losses up to about 20 mc./sec. and which is particularly adapted for use in cores in inductance coils and the like employed in circuits operating at frequencies up to about 20 mc./sec., consisting essentially of substantially homogeneous mixed crystals of nickel-zinc ferrite having an initial magnetic permeability of about 20 to 150 and consisting of the heat reaction product of about 22.5 mol. per cent of NiO, 31.3 mol. per cent of ZnO, and 46.2 mol. per cent of Fe_2O_3, said nickel-zinc ferrite having a Curie point of at least 250° C.

5. A soft ferromagnetic material having low magnetic losses up to about 20 mc./sec. and which is particularly adapted for use in cores in inductance coils and the like employed in circuits operating at frequencies up to about 20 mc./sec., consisting essentially of substantially homogeneous mixed crystals of nickel-zinc ferrite having an initial magnetic permeability of about 20 to 150 and consisting of the heat reaction product of about 34.6 mol. per cent of NiO, 17.2 mol. per cent of ZnO, and 48.2 mol. per cent of Fe_2O_3, said nickel-zinc ferrite having a Curie point of at least 250° C.

6. A soft ferromagnetic material having low

magnetic losses up to about 20 mc./sec. and which is particularly adapted for use in cores in inductance coils and the like employed in circuits operating at frequencies up to about 20 mc./sec., consisting essentially of substantially homogeneous mixed crystals of nickel-zinc ferrite having an initial magnetic permeability of about 20 to 150 and consisting of the heat reaction product of about 24.8 mol. percent of NiO, 31.2 mol. percent of ZnO, and 44.0 mol. percent of Fe_2O_3, said nickel-zinc ferrite having a Curie point of at least 250° C.

7. A process of manufacturing a soft ferromagnetic material having an initial magnetic permeability of about 20 to 150 and low magnetic losses up to about 20 mc./sec. and which is particularly adapted for use in cores in inductance coils and the like employed in circuits operating at frequencies up to 20 mc./sec., comprising the steps of forming an intimate mixture of about 10 to 35 mol. percent of NiO, about 40 to 60 mol. percent of Fe_2O_3, and ZnO in an amount at which mixed crystals of nickel-zinc ferrite are produced having a Curie point exceeding 250° C. and comprising at least 10 mol. percent, sintering the so-formed mixture at a temperature of about 800° to 1300° C in an oxygen-containing atmosphere to form the mixed crystals of nickel-zinc ferrite, and cooling the nickel-zinc ferrite thus obtained in the said atmosphere.

8. A process of manufacturing a soft ferromagnetic material having an initial magnetic permeability of about 20 to 150 and low magnetic losses up to about 20 mc./sec. and which is particularly adapted for use in cores in inductance coils and the like employed in circuits operating at frequencies up to 20 mc./sec., comprising the steps of forming an intimate mixture of about 10 to 35 mol. percent of NiO, about 40 to 60 mol. percent of Fe_2O_3, and about 10 to 31 mol. percent of ZnO, and in an amount at which mixed crystals of nickel-zinc ferrite are produced having a Curie point exceeding 250° C., sintering the so-formed mixture at a temperature of about 800° to 1300° C. in an oxygen-containing atmosphere to form the mixed crystals of nickel-zinc ferrite, and cooling the nickel-zinc ferrite thus obtained in the said atmosphere.

9. A process of manufacturing a soft ferromagnetic material having an initial magnetic permeability of about 20 to 150 and low magnetic losses up to about 20 mc./sec. and which is particularly adapted for use in cores in inductance coils and the like employed in circuits operating at frequencies up to 20 mc./sec., comprising the steps of forming an intimate mixture of about 34 to 36 mol. percent of NiO, about 15 to 18 mol. percent of ZnO, about 48 to 50 mol. percent of Fe_2O_3, and in an amount at which mixed crystals of nickel-zinc ferrite are produced having a Curie point exceeding 250° C., sintering the so-formed mixture at a temperature of about 800° to 1300° C., in an oxygen-containing atmosphere to form the mixed crystals of nickel-zinc ferrite, and cooling the nickel-zinc ferrite thus obtained in the said atmosphere.

10. A process of manufacturing a soft ferromagnetic material having an initial magnetic permeability of about 20 to 150 and low magnetic losses up to about 20 mc./sec. and which is particularly adapted for use in cores in inductance coils and the like employed in circuits operating at frequencies up to 20 mc./sec., comprising the steps of forming an intimate mixture of about 10 to 36 mol. percent of NiO, about 10 to 18 mol. percent of ZnO, about 40 to 50 mol. percent of Fe_2O_3, and in an amount at which mixed crystals of nickel-zinc ferrite are produced having a Curie point exceeding 250° C., sintering the so-formed mixture at a temperature of about 800° to 1300° C., in an oxygen-containing atmosphere to form the mixed crystals of nickel-zinc ferrite, and cooling the nickel-zinc ferrite thus obtained in the said atmosphere.

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