

UNITED STATES PATENT OFFICE

2,636,860

MAGNETIC CORE

Jacob Louis Snoek, Jan Jacobus Went, and Pieter Willem Haayman, Eindhoven, Netherlands, assignors, by mesne assignments, to Hartford National Bank and Trust Company, Hartford, Conn., as trustee

No Drawing. Application April 10, 1946, Serial No. 661,076. In the Netherlands July 6, 1944

Section 1, Public Law 690, August 8, 1946
Patent expires July 6, 1964

6 Claims. (Cl. 252—62.5)

1

This invention relates to magnetic cores containing a ferro-magnetic ferrite as magnetic material. More particularly, the invention relates to magnetic cores for use at low values of magnetic induction, for example in radio, telegraphy and telephony applications.

For various purposes it is of importance to have a material possessing a low value of its longitudinal magnetostriction. As employed throughout the specification this is the absolute value of the magnetostriction.

Thus, for example, a low magnetostriction is one requirement for obtaining low hysteresis losses, such as is desired e. g. for filter coils and Pupin coils. Furthermore, a low magnetostriction is important for attaining a high initial permeability.

The invention permits obtaining very low values of the magnetostriction with ferrites by providing that the ferrite consists of a mixed crystal of a ferrite with positive magnetostriction and a ferrite with negative magnetostriction in a suitable mixing ratio.

For a better understanding of the invention it is pointed out, that, as has now been found, by far the greater part of the ferrites have negative values in regard to magnetostriction. A ferrite with positive magnetostriction is, for instance, magnetite (Fe_3O_4 or $\text{FeO} \cdot \text{Fe}_2\text{O}_3$). By combining ferrites with negative magnetostriction and a ferrite with positive magnetostriction it is possible to obtain mixed crystals of which the values in regard to magnetostriction are between those of the mixed crystal components. By regulating the content of the component with positive magnetostriction it has, according to the invention, been found possible to vary the magnetostriction and to obtain a very low value thereof, either positive or negative, or practically equal to zero.

It is to be noted that, as is well-known, the magnetostriction of a metal acquires very low values at a temperature just below the Curie point. On theoretical grounds this may also be expected in regard to a ferrite. Consequently, this low value of the magnetostriction could be taken advantage of by making use of a ferrite whose Curie point just exceeds the temperature at which the ferrite is used.

Under these circumstances, however, a low magnetostriction is of little use, since just below the Curie point the magnetic saturation has a low value and, in practice, as is well known, the quotient

$$\frac{I_{\max}^2}{\lambda}$$

where $I_{\max}$ is the intensity of the magnetisation

2

at saturation and is defined as the magnetic moment per unit volume, or as the pole strength per unit area both being equivalent and having a unit value of maxwells per square centimeter; and λ is the magnetostriction constant which is a ratio and is the change in length per unit length of a ferromagnetic body which is subject to an external field which will saturate the magnetic material, is more important than the value of λ itself. For instance, the initial permeability of a magnetic material is represented by the formula

$$\mu = \text{const.} \frac{I_{\max}^2}{\lambda \sigma}$$

(Becker and Döring, *Ferromagnetismus*, 1939, page 155) where σ represents the average value of the stresses in the material and is defined as a force per unit area which in the c.g.s. system would have a unit value of dynes per square centimeter.

Furthermore, the use of materials whose Curie point just exceeds the ambient temperature of the material chiefly involves the drawback that the initial permeability just below the Curie point largely depends on the temperature so that such material is unsuitable for practical applications. In fact, the variation of the initial permeability of a ferrite with temperature is usually such that with a decrease in temperature from the Curie point the permeability initially rises very quickly to a maximum and, upon a further decrease in temperature, gradually falls off. In practice, the range in which the permeability largely depends on the temperature will be avoided and for this reason materials will always be used whose Curie temperature is at least to 50°C . Preferably, materials are used having a Curie point between 50 and 250°C . In the present case the expression Curie point is to be understood to mean the temperature at which the initial permeability has dropped to a small fraction of about 10% of the maximum value, or in other words, the temperature at which a magnetic material passes over into a state which can be conceived as having no ferromagnetism for all practical purposes, i. e. the magnetic properties of the material having fallen to such a value that the material is no longer considered ferromagnetic.

By mixed crystal formation of ferrites with positive and negative magnetostriction according to the invention it is now possible to obtain a ferrite having a Curie temperature of at least 50°C , which consequently has a sufficiently high value for $I_{\max}$ in practice and a low value of the

3

magneto-striction in such manner that the absolute value of the quotient

$$\frac{I_{max}^2}{\lambda}$$

is larger than 2×10^{10} .

In the embodiment of the invention in which magnetite is used to constitute the mixed crystal component with positive λ , the content of this component, instead of sintering together a ferrite with negative λ and the ferrite with positive λ in a suitable mixing ratio, or of sintering together a corresponding mixture of the component oxides, is preferably obtained by heating the ferrite with negative λ at a high temperature, for instance 1000°C . and upwards, in a suitable atmosphere, so that a certain quantity of bivalent iron is formed which corresponds to the desired quantity of magnetite; for if in a ferrite a part of the iron passes over, while splitting off oxygen, from the trivalent form into the bivalent, this can be conceived as a formation of Fe_3O_4 in the ferrite. In this embodiment of the invention use is preferably made of a ferrite having a content of more than 50 mol. per cent iron, computed on the basis of Fe_2O_3 i. e. that the mixture, from which this ferrite has been formed by sintering, contained more than 50 mol. per cent of Fe_2O_3 . The excess iron oxide may then serve for the conversion into magnetite; in the absence of an excess there would be a risk, in the formation of bivalent iron, of separation of one or more of the oxides other than Fe_2O_3 constituting the ferrite, so that no homogeneous mixed crystal would ensue.

Theoretically, the atmosphere in which the ferrite is heated should have an oxygen content commensurate with the oxygen pressure with which the ferrite-magnetite mixed crystal to be prepared is in equilibrium at the heating temperature; the heating has to be continued until the ferro-content acquires the desired equilibrium value throughout the ferrite. In practice, however, different reaction conditions will be used, to obtain a suitable product in a reasonable time. When making use of a ferrite of the aforesaid kind having a Fe_2O_3 content exceeding 50 mol. per cent, and heating at temperatures exceeding about 1200°C ., the composition of the atmosphere is relatively unimportant whereas the time and the temperature of the heating are important, provided that the ferrite is not too strongly sintered to compactness so that splitting off of oxygen throughout the ferrite is possible. Care should be taken that during the cooling following the heating operation no interaction can occur between the ferrite and the gaseous atmosphere, due to which the outer layers of the ferrites would acquire a composition different from that of the inner part of the ferrite. Such inhomogeneities may be ascertained by removing the outer part of a ferrite core, for instance, by grinding, and by observation of the modification taking place in the properties of the core. To avoid the formation of a surface layer having a different composition the cooling may take place in an inert, oxygen-poor atmosphere i. e. containing less than 2% of oxygen, for instance nitrogen, or rapid cooling may take place after heating. As an alternative such a possible surface layer may be removed by grinding.

It is pointed out that, as is well-known, several ferrites split off oxygen at a high temperature i. e. that such ferrites have a certain content of bivalent iron. It was not known, how-

4

ever, that the magneto-striction is affected by modification of the ferrous iron content. More particularly with these ferrites the ferrus iron content was not such that

$$\frac{I_{max}^2}{\lambda}$$

exceeded 2×10^{10} throughout the ferrite.

From French patent specification 887,083 it is known to provide, with ferrites, for as high an oxygen content as possible i. e. as small a ferrous iron content of the ferrite as possible in order to reduce the losses of the magnetic material (eddy current, hysteresis- and other losses). Although, according to the invention, in the manufacture of mixed crystals containing magnetite a certain ferrous iron content is provided for it has turned out that, in general, the ferrous iron contents with which the magneto-strictions are low are not so large as to involve losses to a degree rendering the material impracticable particularly at low frequencies e. g. for telegraphy and telephony purposes (Pupin coils, filter coils).

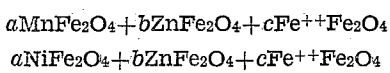
The term "manganese ferrite-forming constituent" is to be understood to include manganese ferrite, and the constituent oxides thereof.

The term "nickel ferrite-forming constituent" is to be understood to include nickel ferrite and the constituent oxides thereof.

The term "zinc ferrite-forming constituent" is to be understood to include zinc ferrite and the constituent oxides thereof.

The term "magnetite-forming constituent" is to be understood to include magnetite and iron oxides capable of forming magnetite.

The ferrous ferrite materials have the formula:



in which the coefficients a , b , and c have values at which

$$\frac{I_{max}^2}{\lambda}$$

exceeds 2×10^{10} and the Curie point is greater than 50°C .

Example 1

A mixture of pure MnO_2 , pure ZnO and pure Fe_2O_3 in a mol. ratio of 25:25:50 is ground for three hours in an iron ball mill. From the mixture, with water as a plastification agent, a rod $100 \times 2 \times 2 \text{ mm}$. is formed at a pressure of 4 tons/cm². The rod is sintered in pure nitrogen for 2 hours at 1300°C . followed by cooling, likewise in nitrogen, down to room temperature in about half an hour. In the same way ferrite rods have been made by using mixtures of the mol. ratio 23:25:52 and 21:25:54. The values of the saturation magneto-striction λ , the saturation magnetisation I_{max} , the quotient

$$\frac{I_{max}^2}{\lambda}$$

the Curie point and the initial permeability of these rods figure in the table below.

$\lambda \cdot 10^6$	I_{max} in c. g. s. units	$\frac{I_{max}^2}{\lambda} \times 10^{10}$	Curie-point in $^\circ \text{C}$.	μ
lot 1, -3.....	250	2	100	1,500
lot 2, -0.4.....	320	25	125	1,900
lot 3, +1.5.....	380	10	150	1,300

5

From the material corresponding with the preparation No. 2 a magnetic annular circuit having an effective permeability of 125 is constructed. At 2000 cycles/sec. and a maximum induction of 7.5 Gauss the value

$$\frac{Rh}{L}$$

for this circuit amounted to 0.24, Rh being the hysteresis resistance of the coil wound on the annular core and L being its self-induction.

Example 2

Three mixtures of pure NiO, pure ZnO and pure Fe_2O_3 in mol. ratios of 15:35:50, 13.8:32.2:54 and 12.6:29.4:58 are formed into ferrite rods similarly to Example 1. The magnetic properties of the materials thus produced are given in the table below, in which the content of bivalent iron is also given.

$\lambda \cdot 10^6$	$I_{\max}$ in c. g. s. units	$\frac{I_{\max}^2}{\lambda} \times 10^{10}$	Curie-point in ° C.	Ferro-content in per cent by weight
lot 1, -2.5-----	300	3.6	150	1.08
lot 2, -0.7-----	350	17.5	200	2.85
lot 3, +4.1-----	400	4	300	5.38

What we claim is:

1. A soft ferromagnetic material consisting essentially of substantially homogeneous mixed crystals of manganese-zinc-ferrous ferrite, said ferrite having the formula:



the coefficients a , b and c being mol fractions and having values at which the Curie point is at least 50° C. and the value of

$$\frac{I_{\max}^2}{\lambda}$$

is at least 2×10^{10} , $I_{\max}$ being the magnetization flux at saturation in maxwells per cm^2 and λ being the magnetostriction value in change in length per unit length of the material.

2. A soft ferromagnetic material consisting essentially of substantially homogeneous mixed crystals of nickel-zinc-ferrous ferrite having the formula:



the coefficients a , b , and c being mol fractions and having the values at which the Curie point is at least 50° C. and the value of

$$\frac{I_{\max}^2}{\lambda}$$

is greater than 2×10^{10} , $I_{\max}$ being the magnetization at saturation in maxwells per cm^2 and λ the magnetostriction value in change in length per unit length of the material.

3. A process of manufacturing a soft ferromagnetic material comprising the steps of mixing a manganese ferrite-forming constituent, a zinc ferrite-forming constituent, and a magnetite-forming constituent in amounts expressed in terms of mol percents of MnO_2 , ZnO , and Fe_2O_3 of about 21 to 25, 25 and about 50 to 54, and producing upon sintering substantially homogeneous mixed crystals of manganese-zinc-ferrous ferrite having a bivalent iron content at which

$$\frac{I_{\max}^2}{\lambda}$$

exceeds 2×10^{10} , $I_{\max}$ being the magnetization flux

6

at saturation in maxwells per cm^2 and λ being the magnetostriction value in change in length per unit length, sintering the mixed constituents at a temperature of about 1000° to 1300° in an inert oxygen-poor atmosphere for a sufficient time to produce said mixed crystals, and cooling the mixed crystals in said atmosphere.

4. A process of manufacturing a soft ferromagnetic material comprising the steps of mixing a nickel ferrite-forming constituent, a zinc ferrite-forming constituent, and a magnetite-forming constituent in amounts expressed in terms of mol. percentages of NiO , ZnO and Fe_2O_3 of about 12.6 to 15, 29.4 to 35, and 50 to 58 and producing upon sintering substantially homogeneous mixed crystals of nickel-zinc-ferrous ferrite having a bivalent iron content at which

$$\frac{I_{\max}^2}{\lambda}$$

exceeds 2×10^{10} , $I_{\max}$ being the magnetization flux at saturation in maxwells per cm^2 and λ being the magnetostriction value in change in length per unit length, sintering the mixed constituents at a temperature of about 1000° to 1300° C. in an inert oxygen-poor atmosphere for a sufficient time to produce the mixed crystals, and cooling the mixed crystals in said atmosphere.

5. A process of manufacturing a soft ferromagnetic material comprising the steps of mixing about 21 to 25 mol. per cent of MnO_2 , about 25 mol. per cent of ZnO , and about 50 to 54 mol. per cent of Fe_2O_3 , sintering the mixture at about 1300° C. in an inert oxygen-poor atmosphere for a sufficient time to form substantially homogeneous mixed crystals of manganese-zinc-ferrous ferrite having a bivalent iron content at which

$$\frac{I_{\max}^2}{\lambda}$$

exceeds 2×10^{10} , $I_{\max}$ being the magnetization flux at saturation in maxwells per cm^2 and λ the magnetostriction value in change in length per unit length, and cooling the mixed crystals in said atmosphere.

6. A process of manufacturing a soft ferromagnetic material comprising the steps of mixing about 12.6 to about 15 mol. per cent of NiO , about 29.4 to about 35 mol. per cent of ZnO , and about 50 to about 58 mol. per cent of Fe_2O_3 , sintering the mixture at about 1300° C. in an inert oxygen-poor atmosphere for a sufficient time to form substantially homogeneous, mixed crystals of nickel-zinc-ferrous ferrite having a bivalent iron content at which

$$\frac{I_{\max}^2}{\lambda}$$

exceeds 2×10^{10} , $I_{\max}$ being the magnetization flux at saturation in maxwells per cm^2 and λ magnetostriction value in change in length per unit length, and cooling the mixed crystals in said atmosphere.

JACOB LOUIS SNOEK.

JAN JACOBUS WENT.

PIETER WILLEM HAAYMAN.

References Cited in the file of this patent

UNITED STATES PATENTS

Number	Name	Date
1,946,964	Cobb -----	Feb. 13, 1934
2,452,529	Snoek -----	Oct. 26, 1948
2,452,530	Snoek -----	Oct. 26, 1948