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Deschamps et al.

[11] **3,855,691**

[45] **Dec. 24, 1974**

[54] METHOD OF MAKING A MAGNETIC MATERIAL PART WITH SPATIAL DISTRIBUTION OF THE PERMEABILITY

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Mar. 28, 1972 France 72.10779

[52] **U.S. Cl.** **29/608,** 252/62.57, 252/62.62, 336/233

[51] **Int. Cl.** **H01f 3/08**

[58] **Field of Search** 29/608, 607, 602; 252/62.56, 62.57, 62.62; 336/233

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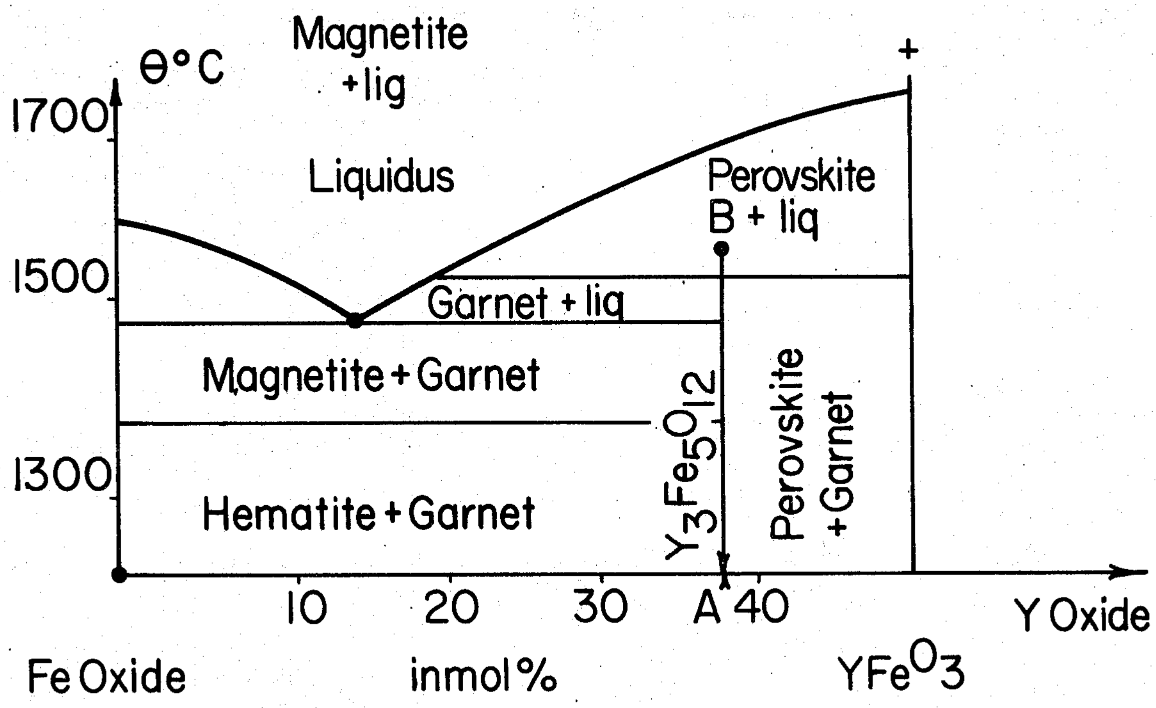
Primary Examiner—Carl E. Hall
Attorney, Agent, or Firm—Kemon, Palmer & Estabrook

[57] ABSTRACT

A part made of ferrimagnetic material with a spatial variation of the permeability value is obtained through heat treatment of a body of ferrimagnetic material at the temperture such that the free energy of the material is low and that a transformation into a material with higher free energy is obtained, stopping said heating before complete transformation and further machining of the part. The heat treatment is carried out under reduced pressure when a liquid phase develops at the heating temperature. When solid phase is maintained the body is heated in presence of a metal salt or oxide.

10 Claims, 14 Drawing Figures



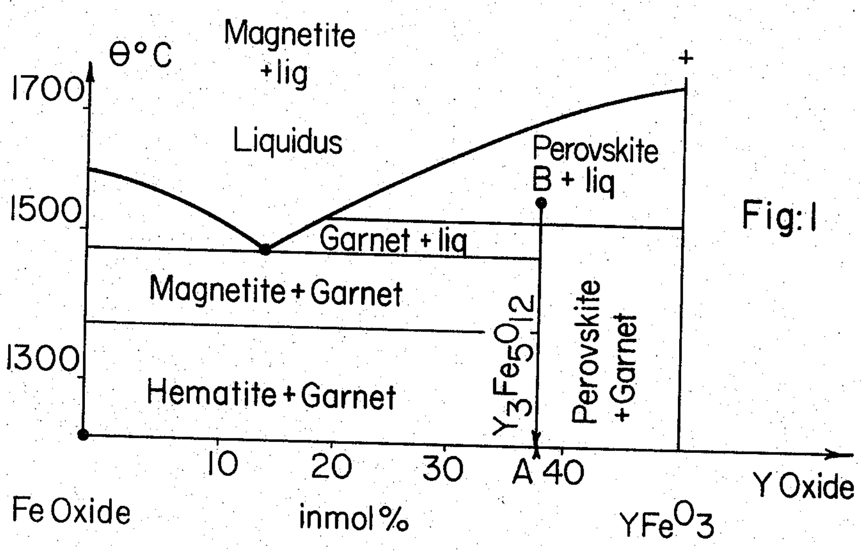

θ°C
1700
1500
1300
Magnetite +lig
Liquidus
Perovskite B + liq
Garnet + liq
Magnetite + Garnet
Hematite + Garnet
$Y_3Fe_5O_{12}$
Perovskite +Garnet
10
20
30
A
40
Y Oxide
Fe Oxide
inmol %
YFe^{O_3}

Fig: 1

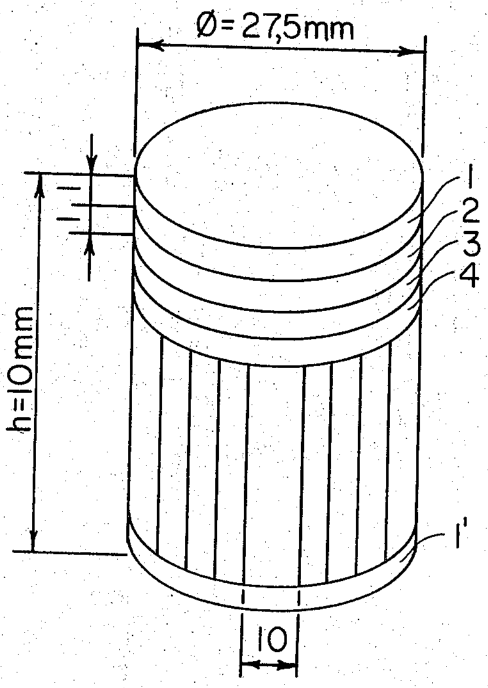

Ø = 27,5mm
1
2
3
4
h=10mm
1'
10

Fig: 3

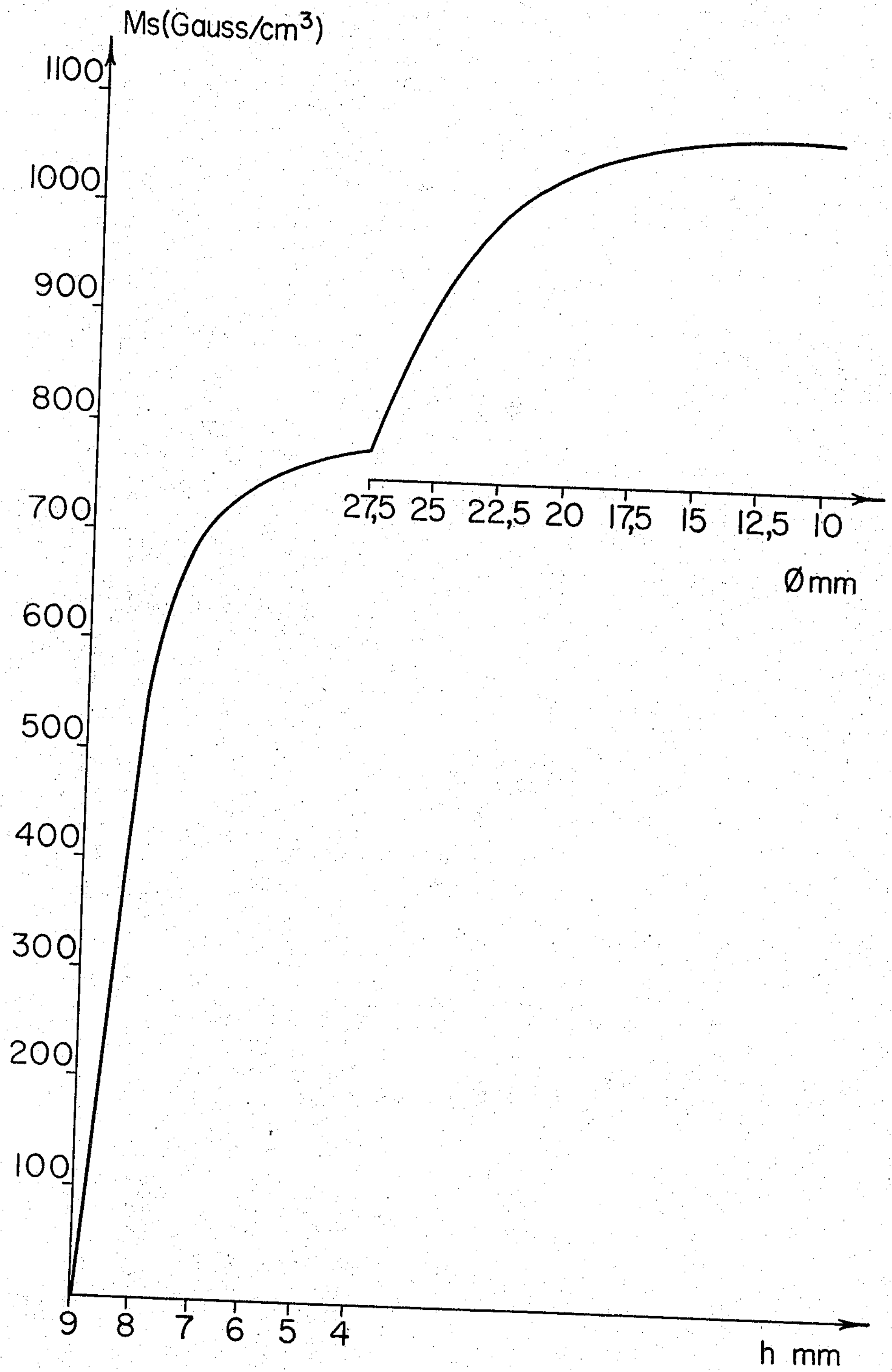

Ms(Gauss/cm³)
1100
1000
900
800
700
600
500
400
300
200
100
27,5
25
22,5
20
17,5
15
12,5
10
Ø mm
9
8
7
6
5
4
h mm

Fig: 2

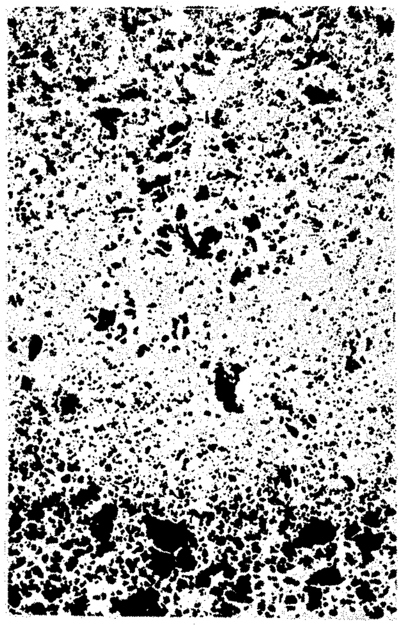


FIG. 4

FIG. 5

FIG. 6

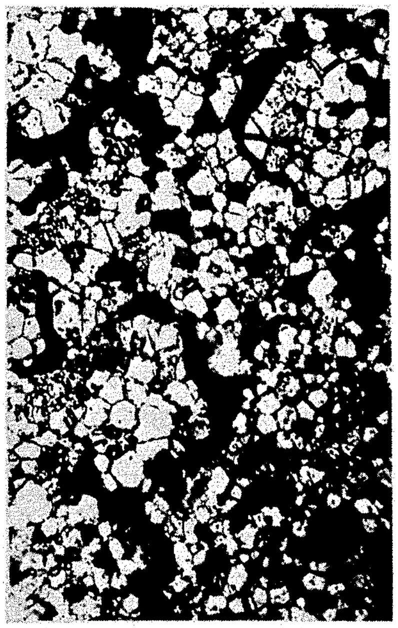


FIG. 7

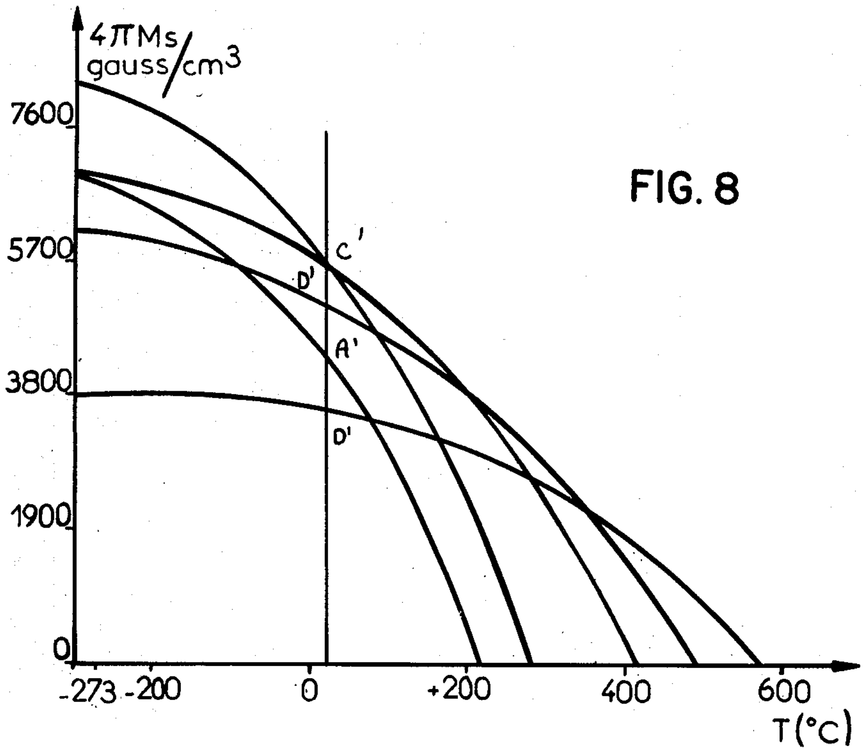


FIG. 8

FIG. 9

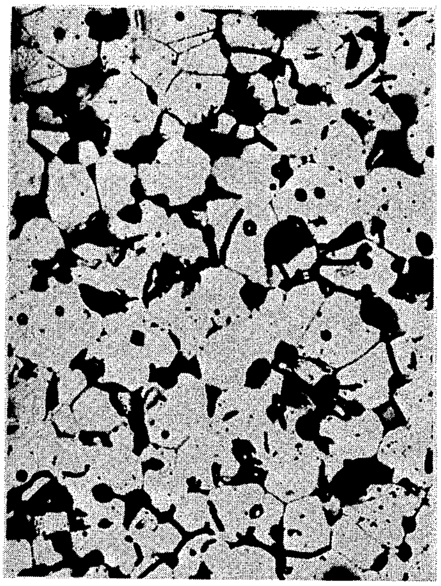


FIG. 10

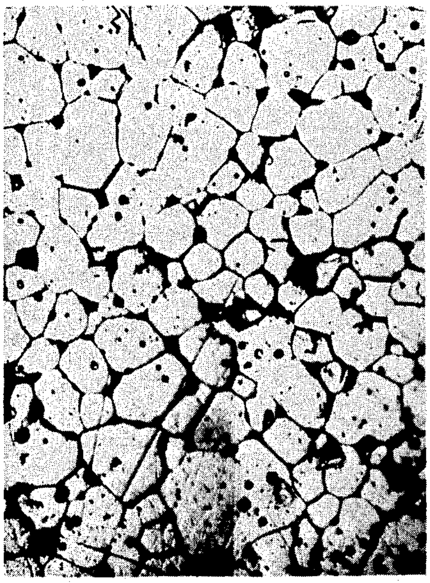


FIG. 11

FIG. 12

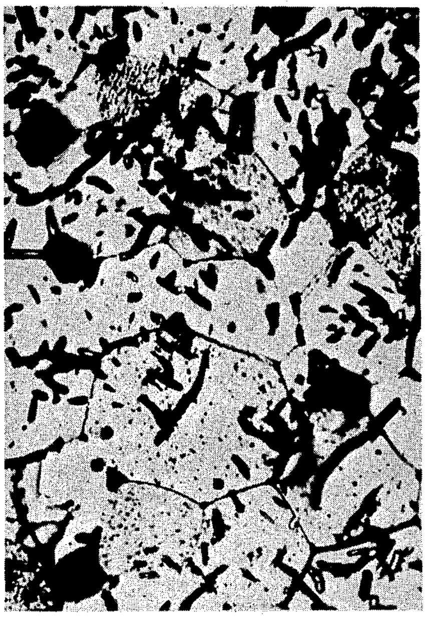


FIG. 13

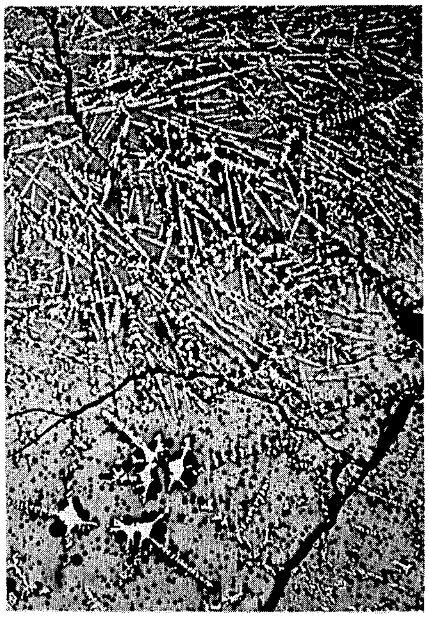


FIG. 14

METHOD OF MAKING A MAGNETIC MATERIAL PART WITH SPATIAL DISTRIBUTION OF THE PERMEABILITY

SUMMARY OF THE INVENTION

The present invention concerns a process for the preparation of homogeneous articles of the ceramic type, of which the magnetic properties vary from point to point. Magnetic circuits whose permeability varies spatially are usually built up of different materials chosen for the appropriate value of their permeability. However, the assembly of various materials may present disadvantages and/or difficulties, for instance when the dimensions of the articles are small or when it is likely to be subjected to such temperature differences that harmful stresses will develop in the assembly of materials due to differences in expansion coefficients. In addition, such applications as substrates for microwave integrated circuits require continuity of other physical properties for impedance constancy, which is not provided by an assembly of parts made of different materials.

According to the present invention, the whole article is made of a single material whose magnetic properties are locally modified by an appropriate thermal treatment of a piece of material with a permeability value corresponding to one of the required values and further machining of said piece to obtain the required spatial distribution.

BACKGROUND OF THE INVENTION

In solid state physics, it is standard practice to reproduce the desired spatial distribution of conductivity in an article made of a semiconductor material by providing local diffusion of doping impurities in its crystal lattice. The phenomenon most commonly employed is that of the introduction of an impurity into the lattice referred to as in-diffusion. Evaporation of an impurity from the lattice is also used and called out-diffusion. The invention uses both types of diffusion as applied to materials which consist of an aggregate of crystallites.

It is well known that the magnetic properties of materials relies on the algebraic sum of the spins of the ions distributed between the various crystallographic sites. When this sum is zero, the material is non-magnetic (its permeability is near that of the vacuum). Change of ion in the sites may change the value of the sum and therefore of the permeability. In practice, soft magnetic materials have been obtained essentially from structures of the spinel type, that is to say, those belonging to the space group O_h^7 F 3 dm, and from structures of the garnet type, belonging to the group O_h^{10} 1 a 3 d.

From the physico-chemical viewpoint, the change may be summed up either as a suppression of ions from some sites, as the introduction of foreign ions into the lattice or as a substitution of ions at some of the lattice sites. The second case will not be taken into consideration due to the fact that too little vacancies are available in current soft magnetic materials for easy fill up of the lattice introducing an important change in the magnetic properties. The invention therefore is based on the first and third type of modifications. According to the invention, the first case consisting of locally depriving the lattice of ions through heating the material will be used when the phase diagram of the material shows the formation of a liquid phase corresponding to a chemical composition differing from that of the solid and the third case is achieved through solid phase diffusion of a salt or oxide of the substituting ion into the magnetic material. The ion substitution may assume two apparently different aspects; in the first, the substitution of a foreign metallic ion for an ion previously existing in the structure does not modify the chemical composition and may result in a deformation of the crystal lattice, and the ion driven off is accumulated in the form of an oxide or of another salt at the grain boundaries; in the second, the substitution reaction is accompanied by a modification of chemical composition since the previous ions are evaporated as oxide or salt or the substitution is only a change in the valency of a polyvalent metal (such as iron for instance) with evaporation of molecules corresponding to the anions of the lattice.

The structural changes within the lattice of the material are based on thermodynamic equilibrium as is briefly summarized below. In fact, these two aspects are different embodiments of the same physico-chemical mechanism.

For any stable chemical composition at the temperature T under consideration, the free energy of the material is given by the absolute value of the expression:

$$E = U - TS \qquad (1)$$

where U is the internal energy, S is the entropy, and T is the absolute temperature. If the vibration energy and the magnetic interaction energy are disregarded, U appears as the sum of:

U_i = electrostatic energy

U_r = Born's elastic repulsion energy

U_e = covalent bond energy

As is known, entropy is linked to the presence of disorder (S is low for a highly ordered structure); since a temperature rise results in a reduction of the order of the crystal lattice (specially if a liquid phase develops), the entropy increases with the temperature. The product TS therefore increases with temperature. In order to evaluate U, it is necessary to make an hypothesis on the nature of the material. Let us consider, for example, a spinel. The general formula of spinels indicating the distribution of the metallic ions between the tetrahedral sites A (8 metallic ions per mesh) and the octahedral sites B (16 metallic ions per mesh), is written:

$$\underbrace{Fe_{2\lambda}\ M_{(1-2\lambda)}}_{\text{Tetrahedral Sites A}} \qquad \underbrace{Fe_{2-2\lambda}\ M_{2\lambda}\ O_4}_{\text{Octahedral sites B}}$$

where M represents a bivalent ion. The position of the **32** oxygen ions is fixed by the parameter δ as defined in the international crystallographic tables. The unit cell of such a spinel structure is shown and explained at page **115** in the book entitled "Microwave ferrities and ferrimagnetics" by Lax and Button published by Mac Graw Hill in **1962.**

The electrostatic energy U_i of a spinel is expressed as a function of the distribution of the ions between the sites A and B (parameter λ) and of the position of the oxygens (parameter $u = 3/\mathbf{8} + \delta$). λ and δ are determined for each structure by X-ray analysis. The usual values of δ are comprised within the range ($0 < \delta < 0.01$). The repulsion energy U_r can be calculated from the Born-Mayer formula. The covalence energy U_e is zero in the absence of a covalent bond. When covalent bonds exist, U_e may be high and, as a result of the decrease of the ionic charge, it may become the preponderant factor of U.

In the case of garnets, the internal energy is also linked to the structure. However a different phenomenon occurs due to the phase diagram of yttrium and iron oxides the system (yttrium iron garnet) shown on FIG. 1 as published in the Journal of the American Ceramic Society, volume 5, no. 44, page 213.

If a garnet material (supposed stoichiometric in composition) is heated, the material will follow line AB of the diagram at the crossing of the liquidus horizontal line ($T = 1510°$ C). E is quite small. If the free energy of perovskite is considered at the same temperature (line CE), no liquid phase is present and the free energy is much higher. This explains that a structural change occurs spontaneously part of the garnet being changed into perovskite. From the chemical viewpoint this change can be written as:

$$\underset{\text{(garnet solid)}}{3\ Y_2O_3\ 5\ Fe_2O_3} \longrightarrow \underset{\text{(perovskite solid)}}{3\ Y_2O_3\ 3\ Fe_2O_3} + \underset{\text{(liquid)}}{2\ Fe_2O_3}$$

Since the heating energy is high enough, reduction of the liquid iron oxide occurs simultaneuosly:

$$\underset{\text{(liquid)}}{3Fe_2O_3} \longrightarrow \underset{\text{(liquid)}}{2FeO} + \underset{\text{(liquid)}}{2Fe_2O_3} + \tfrac{1}{2}O_2 \nearrow$$

As shown one out of three trivalent iron ions becomes divalent. These divalent ions give birth to a spinel structure Fe_2O_3FeO which is liquid and therefore has a small free energy value. The two last reactions do not cooperate in an high proportion to the free energy of the material at point B. The free energy at B of the liquid garnet phase is much smaller than the free energy at the same temperature of the solid perovskite phase.

According to the invention the change in the magnetic properties of a magnetic material F_1 is obtained by heating a piece of said magnetic material at a temperature such that the free energy of the F_1 material is much smaller than the free energy of another ferrimagnetic material F_2 into which F_1 is transformed at said temperature, this change is stopped before it has been carried out completely and the piece of material is machined so that at least one part of the outer surface of said machined piece consists of the initial F_1 material.

According to a first variant of the invention, a body of a material of complex structure having the magnetic properties required to constitute a fraction of the solid magnetic article is subjected to a thermal treatment in vacuo at a temperature several degrees higher than the solidus-liquidus equilibrium temperature that is at a temperature where the free energy is near zero for a period such that the magnetic properties of the external fraction of the body only are modified by evaporation of the liquid phase, the initial magnetic properties of the central fraction of the body being retained. By subsequent machining of the body thus treated, there can be obtained a mechanically solid magnetic article having the desired space distribution of permeability values. The application of a thermal treatment in vacuo facilitates the evaporation of the liquid phase formed. The use of a temperature which is several degrees higher than the temperature at which the liquid phase is formed renders possible a gradual transformation of the structure of the material which retains the mechanical cohesion of the body. This variant corresponds roughly to an out-diffusion according to solid state physics terminology since the liquid phase which is evaporated carries of some of the lattice ions and thereby changes the sum of the spins in the lattice. Sometimes further chemical changes simultaneously occur as explained with reference to the yttrium, iron oxides diagram.

According to a second variant of the invention in solid phase, a diffusion is effected in a crystal structure of an initial magnetic material, that is to say, the replacement of an ion M_1 in one site by a different ion M_2 corresponding to a second structure of magnetic material by heating the material in presence of a M_2 salt or oxide at a temperature such that $E_1 < E_2$, where E_1 is the internal energy of the initial material ($M_1\ Fe_2O_4$), and E_2 is the energy of the second material ($M_2Fe_2O_4$), and such that E_1 is very low. In order terms, $U_2 - TS_2 > U_1 - TS_1$. Experience has shown that this temperature is higher than 850° C for the spinels usually used as soft magnetic materials and about 1200° C in the case of garnets.

As will be apparent from the following description of the examples, the thermal treatment may have the effect of increasing or reducing the permeability of the material, depending upon the initial composition of the latter. Similar treatments may have either effect. The temperature of the thermal treatment is fixed by the above conditions for the free energy. In case of the liquid phase intermediate it can be selected on the phase diagram of the constituents of the body. The application of a reduced pressure in the course of the thermal treatment generally results in a reduction of the temperature at which the liquid phase is formed, as compared with its value at atmospheric pressure. This point is particularly favourable to maintenance of the mechanical cohesion of the body.

DETAILED DESCRIPTION OF THE DISCLOSURE

The invention will be readily understood from the following description, which is given by way of non-limiting illustration, and with reference to the accompanying figures, in which:

FIG. **1** is a known phase diagram of the mixture of iron and yttrium oxides,

FIG. **2** shows experimental curves representing the value of the saturation magnetisation as a function of the space co-ordinates of a cylindrical block of an iron-yttrium-aluminium-gadolinium garnet treated in accordance with the invention,

FIG. **3** is a diagram of the block of material corresponding to the above curve,

FIGS. **4** to **7** inclusive are micrographic views of different sections of the material from which the curves of FIG. **2** were obtained,

FIG. **8** is a diagram representing the saturation magnetisation of ferrites of Ni and Zn as a function of the composition, and

FIGS. **9** and **10** are micrographs of a specimen of Ni-Zn ferrite treated in accordance with the invention,

FIG. **11** is a nickel ferrite specimen which has undergone a heat treatment, FIGS. **12**, **13** and **14** are micrographs of the same nickel ferrite after it has undergone a diffusion of Cu^{++}, Zn^{++} and B^{++} ions respectively under the same heat treatment.

The invention will first be described as applied to an yttrium-iron garnet containing aluminium and gadolinium, of a type marketed under No. 6,905 by the Applicants. This material, which is green in colour, has good magnetic properties ($4\pi Ms$ of the order of 900 to 1,000), and is particularly adapted to operate in the frequency range of **9** GHz (linewidth between 70 and 80 oersteds — tangent of the loss angle of the order of 10^{-4}). It is commonly used in the production of circulators, isolators, etc., based upon the propagation of electromagnetic microwaves in a high-permeability material. It is well known to every specialist that the use of such a garnet as a substrate for integrated microwave circuits is hindered by disadvantages which could be at least partially eliminated by a reduction of the permeability of the ferrite at the places where no magnetic field is applied. The geometrical distribution of the permeability values depends, of course, upon the design of circuit to be produced.

As already mentioned, FIG. **1** shows the phase diagram, at atmospheric pressure, of the iron oxide-yttrium oxide mixture, as published in the Journal of American Ceramic Society - 1961 — Vol. 5, No. 44, page 213. The quaternary diagram of the iron-yttrium-gadolinium-aluminium oxide mixtures cannot be represented in a simple form on the same diagram. Since aluminium oxide is more refractory than iron and yttrium oxides the appearance of an aluminium-rich liquid phase takes place only at temperature higher than those at which the iron (or yttrium) oxide liquid phase appears. At the temperatures indicated in the diagram of FIG. **1**, the presence of the other two constituents has scarcely any effect on the phase diagram. In accordance with the present invention, there is employed as the initial material a solid body, for example of cylindrical form, consisting of a garnet obtained by any known method, such as for instance by that described in the British application filed by the Applicants on the Feb. 2nd, 1973 for: "Improved production process of fine grained ferrites," which body is coated in alumina powder and disposed in a vacuum oven whose temperature is brought to 1,300° C after out-gassing for about 1 hour at a pressure of 10^{-5} cm.Hg. The temperature rise takes place in about 15 minutes. The garnet follows a course similar to AB on the phase diagram. At the point B, there are present a solid phase consisting of garnet transformed into perovskite (or orthoferrite) and a liquid phase consisting essentially of iron oxide. At 1,290° C, there is noted the appearance of a liquid phase which is at least partially absorbed by alumina. The temperature is maintained for 3 hours at 10° C above the point at which the liquid phase appears. The oven is then cooled by natural cooling (about 2 hours). When the body is removed from the oven, it is found that the colour of the external layer has become brownish-red, which clearly corresponds to the colour of perovskite.

The curves of FIG. **2** show the variation of the saturation magnetisation of the body subjected to two successive series of machining operations, the first being a plane grinding having the effect of eliminating fragments parallel to the base of the cylinder and reducing the height of the body, while the second is a cylindrical grinding having the object of eliminating a cylindrical film and reducing the diameter of the body.

FIG. **3** illustrates these successive operations. The overall saturation magnetisation of the article after thermal treatment is 170 gauss/cm^3. In the course of a first series of steps, discs such as **1**, **2**, etc. in a direction parallel to one of the terminal faces of the cylinder are successively eliminated. These successive discs have a thickness of 1 mm. The initial height of the article is 10 mm and its diameter is 2.75 mm. As will be apparent from FIG. **2**, the elimination of a fragment of 1 mm, such as the fragment **1'** at one of the ends of the cylinder results in a considerable increase in the saturation magnetisation, which changes to 735 gauss/cm^3 (origin of the curve $h=9$ mm). The successive eliminations of fragments of 1 mm, such as **1**, **2**, **3**, **4**, results in the case of the following two fragments in an increase of the saturation magnetisation, which changes to 745 gauss/cm^3 for 6 mm, and 775 gauss/cm^3 for 5 mm, respectively. It consequently appears clear that the first fragments eliminated had no magnetic property, the high increase in the saturation magnetisation being a result of a reduction in volume due to elimination of a non-magnetic fraction of this body. The elimination of the successive fractions continues to increase the saturation magnetisation, but in much smaller proportions, which would tend to show that the volume of the material eliminated has a permeability lower than maximum permeability. The elimination of the last section, bringing the height of the body to 4 mm, even results in a levelling out of the saturation magnetisation, taking into account the precision of the measurements. This result would tend to indicate that the material removed in the course of this last operation has a mean permeability similar to that of the remaining body. It will be observed that this last section reaches the centre of the treated cylindrical body. A second series of steps was carried out on the same body by cylindrical grinding of the remaining body, i.e. by reduction of the diameter. The results obtained are shown in the upper part of the curve of FIG. **2**. As will be apparent, the elimination of the external zone of the cylinder results in an appreciable increase in the saturation magnetisation, which confirms that only material of low permeability has been removed. With an initial diameter of 27.5 mm, a saturation magnetisation of 760 gauss/cm^3 was measured. The saturation magnetisation measured is 850 gauss/cm^3 for a diameter of 25.5 mm. The measurements made at 23.5 mm and 21.5 mm give values of 777 and 1030 gauss/cm^3. The last measurement made on the article reduced to a diameter of 10 mm gives a saturation magnetisation of 1,060 corresponding to the value of the saturation magnetisation of the garnet before heat treatment. The curve of FIG. **2** therefore shows the superficial modification of the permeability by heat treatment of the garnet and the possibility of maintaining in a part of a solid body the initial values, while notably modifying the permeability values in a peripheral zone. The experimental results just described thus make it possible to obtain, by plane grinding of cylindrical articles, discs of homogeneous material whose centre, of green colour, has the magnetic characteristics of the garnet, and in which a red-coloured peripheral zone has low permeability and good dielectric properties. The mechanical characteristics of the wafer thus obtained are entirely similar to those of a garnet wafer.

FIG. **4** is a micrographic view of the section of the body of FIG. **2** before the heat treatment, with a magnification of 50. The lower part corresponds to the peripheral zone and has relatively coarse grains. The central part of the micrograph corresponds to a bright zone and the upper part corresponds to the centre of the body and to a green zone. Larger-scale micrographs of the three zones appearing in FIG. **4** form the subject of FIGS. **5, 6** and **7,** which correspond respectively to the peripheral zone, to the bright intermediate zone and to the central zone. The magnification of these micrographs is 1,000. As will be apparent, the dimensions of the grains constituting the peripheral zone are much greater than those of the grains constituting the central zone. The black portions of the photographs correspond to grains torn out in the course of the polishing treatments and to the chemically attacked grain junctions. The average dimensions of the grains change from 20 microns in the peripheral zone to 5 – 6 microns in the central zone. There will be observed in the central zone continuous dark paths which may be interpreted as diffusion channels and which would tend to show that the heat treatment carried out has started to modify the core of the body. There is observed in the course of the heat treatment an evaporation of a liquid iron oxide phase progressively absorbed by the alumina powder in which the body is buried.

In the example just described, the out-diffusion of one of the constituents of the ferrite is accompanied by the disappearance of the magnetic properties of the material. The out-diffusion of one of the constituents of different magnetic material may result in an increase in the permeability or merely a partial reduction thereof. The following example belongs to the latter category. The family of curves of FIG. **8** represents the saturation magnetisation, $4\pi Ms$ in gauss/cm^3 as a function of the temperature in degrees C, for zinc nickel ferrites of the family:

$$Ni_{1-\delta}\ Zn_{\delta}\ Fe_2O_4$$

for various compositions (variation of δ between 0.65 and 0.00). This diagram is taken from the book "Les ferrites" by Smit and Vijn, published in 1959 by Philips Technical Library, p. 158.

As will be seen, at 20° C (points A', B', C', D'), the saturation magnetisation varies with the zinc concentration. When the starting material contains 65 percent of Zn (point A'), the reduction in the ZnO content results in a slight increase in the saturation magnetisation (points B' and C'), followed by a reduction (point D' corresponding to pure Ni ferrite). The following experiments have shown that in fact the reduction of ZnO content which can be obtained by thermal treatment in vacuo of the material results, in accordance the heating temperature, in a rearrangement of the structure of the ferrite, accompanied by an elimination of oxygen or ferric oxide. The two following experiments were carried out on a ferrite corresponding to the point B' of the diagram at $\delta = 0.2$.

In a first experiment, the ferrite is heated in vacuo for 2 hours between 1,100° and 1,250° C in an alumina crucible. There is observed in the course of the thermal treatment aliberation of zinc oxide vapour and a liberation of oxygen. The reaction may be written as follows:

$$0.8NiO,\ 0.8Fe_2O_3,\ 0.2ZnO,\ 0.2Fe_2O_3 \longrightarrow 0.8NiO,\ 0.8Fe_2O_3,\ 0.133Fe_3O_4,\ 0.2\overset{\nearrow}{ZnO},\ 0.068\overset{\nearrow}{O_2}$$

The starting ferrite has a saturation magnetisation of 4760 gauss/cm^3, which value is reduced to 3800 gauss/cm^3 after the thermal treatment. The measured loss angles show that the body thus obtained cannot be used in a microwave circuit owing to the presence of Fe_3O_4.

When the same ferrite is heated to temperatures between 1,270° and 1,310° C, there is observed an evaporation of zinc oxide, followed by the appearance of a liquid iron oxide phase, which evaporates. The reaction then occurring is the following:

$$0.8NiO,\ 0.2ZnO,\ Fe_2O_3 \longrightarrow 0.8NiO,\ 0.8Fe_2O_3 + 0.2\overset{\nearrow}{ZnO},\ 0.2\overset{\nearrow}{Fe_2O_3} \qquad (2)$$

and there are in fact obtained, after thermal treatment, approximately the characteristics of the pure nickel ferrite both for the value of the saturation magnetisation (3,600 gauss/cm^3) and for that of the losses.

Experience has shown that heating above the temperature defined in the second experiment also degrades the characteristics of the product obtained, owing to the formation of Fe_3O_4.

In a first series of substitution experiments, the initial material is a nickel ferrite of spinel structure, $NiFe_2O_4$, in which $2\ \lambda = \mathbf{1}$, the nickel ions occupying only the octahedral sites B. Cupric ions are diffused into this structure under the following conditions: after sintering and optional grinding, the spinel is disposed in a non-porous sintered and crystallised alumina boat provided with a lid. A few grammes of copper oxide CuO are added and the temperature is raised to 900° C and maintained for 48 hours. The saturation magnetisation of the material after treatment is substantially nil. Using the above notations, it is known that copper oxide $CuFe_2O_4$ has a structure such that $2\lambda = 0.88$ and $\delta = 0.005$. The copper ions occupy the octahedral sites in a majority, and they have strong square covalent bonds in the spinel structure, which even produce a quadratic deformation of the mesh. The covalence energy of copper is therefore very high. Nickel ferrite does not exhibit any covalent bonds. If the nickel ferrite is denoted by F_1 and the copper ferrite by F_2, then at 900° C E_1 is in the neighbourhood of zero, while the free energy E_2 is distinctly higher.

In the course of the substitution reaction, the nickel ions become concentrated in the form of oxide in the grain boundaries. In another series of substitution experiments, nickel ferrite was treated under the same conditions at 1,250° C for 48 hours in the presence of zinc oxide. There was again obtained a substitution of the nickel ions by zinc ions. Under the above conditions, an increase of the saturation magnetisation of the nickel ferrite from 3,300 to 4,300 gauss/cc was obtained. It is known that, in zinc ferrite, the zinc ions occupy the tetrahedral sites A ($2\lambda = 0$), while the nickel ions of the initial structure occupy the sites B. The diffusion is therefore accompanied by a transfer of the metallic ions in addition to their substitution. The zinc ions in the final structure exhibit strong tetrahedral covalent bonds, which explains why the free energy of the zinc ferrite is higher at 1,250° C than that of nickel ferrite. Account must also be taken, in evaluating the free energy, of the energy variation resulting from the transfer of the ions between the sites B and A, which variation may be evaluated, as a first approximation, by the electrostatic energy difference between a normal and an inverted spinel (cf the above mentioned book by Lax and Button page 115).

The same nickel ferrite was subjected to the same experimental conditions in the presence of boron oxide and heated at 1,300° C for 48 hours. The saturation magnetisation changed from 3,300 gauss/cc to 2,460 gauss/cc. In this diffusion, the substitution is accompanied by a modification of the chemical composition by formation of boroferrite of the formula $B_2O_3Fe_2O_3$ 2 NiO.

Owing to the low value of the ionic radius of boron, the electrostatic attraction forces are higher than in the case of nickel. The component U_i of the internal energy is increased at a given temperature, which clearly corresponds to a value of $E_2 > E_1$. The diffusion temperature is so chosen that the nickel ferrite has under these conditions a low internal energy. The micrograph shows that the grain junctions have substantially disappeared. The magnification of the latter micrograph is 150, and that of the preceding ones 1,000.

The yttrium-gadolinium-aluminium garnet marketed under the number 6905 by the Applicants, and having a saturation magnetisation of 850 gauss/cc, was treated for 48 hours at 1,300° C in a closed boat in the presence of boric oxide. After treatment, the saturation magnetisation had become 400 gauss/cc. This diffusion is accompanied, as in the previous case, by a change of chemical composition due to formation of yttrium borate YBO_3. As in the previous case, the electrostatic energy of the borate is substantially higher than that of the garnet. The free energy of the second ferrite is therefore considerable.

The foregoing examples describe diffusion treatments with oxide. Salts such as chlorides or nitrates may also be used. However, it is often simpler to choose oxides so as to avoid the development of highly reactive gas which may accompany the decomposition of the salts.

What we claim:

1. A process for the manufacture of a solid magnetic article with a spatially uneven distribution of permeability which comprises:

- providing a sintered solid piece of polycrystalline magnetically uncompensated initial F_1 material having a first permeability value,
- heating said sintered solid piece at a temperature such that the free energy of said F_1 material is smaller than the free energy of another ferrimagnetic F_2 material having a second permeability value different from said first permeability value,
- transforming at said temperature a portion of said F_1 material into said F_2 material,
- discontinuing said heating before the material of said piece is completely transformed into F_2 material, and
- machining the resulting piece containing both F_1 and F_2 material so that at least one part of the outer surface of the machined piece consists of F_1 material.

2. A process for the manufacture of a solid magnetic article with a spatially uneven distribution of the permeability according to claim **1** in which a liquid phase of different chemical composition develops at the heating temperature, the chemical composition of which differs from that of the initial I_1 material.

3. A process according to claim **2** in which said heating is made under reduced pressure.

4. A process for the manufacture of a solid magnetic article with a spatially uneven distribution of permeability according to claim **3** in which said initial F_1 material is an yttrium iron Gd, Al substituted garnet and said heating temperature is between 1,250° and 1350° C.

5. A process for the manufacture of a solid magnetic article with a spatially uneven distribution of permeability according to claim **3** in which said initial F_1 material is a Ni - Zn spinel ferrite and said heating temperature is between 1,270° and 1,310° C.

6. A process for the manufacture of a solid magnetic article with a spatially uneven distribution of the permeability according to claim **1** in which said heating is carried on at a temperature lower than the liquefaction of the F_1 material in presence of a salt of a foreign metal which constitutes the F_2 material through substitution.

7. A process for the manufacture of a solid magnetic article with a spatially uneven permeability distribution according to claim **6** in which said initial material is nickel spinel, the metal ion of said salt of foreign metal is divalent zinc and said heating temperature is above 850° C.

8. A process for the manufacture of a solid magnetic article with a spatially uneven permeability distribution according to claim **6** in which said initial material is nickel spinel, the metal ion of said salt of foreign metal is divalent copper and said heating temperature is above 850° C.

9. A process for the manufacture of a solid magnetic article with a spatially uneven permeability distribution according to claim **6** in which said initial material is nickel spinel, the metal ion of said salt of foreign metal is divalent boron and said heating temperature is above 850° C.

10. A process for the manufacture of a solid magnetic article with a spatially uneven permeability distribution according to claim **6** in which said initial material is an yttrium-iron garnet the metal ion of said salt of foreign metal is divalent boron and said heating temperature is above 1,200° C.

* * * * *

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,855,691 Dated December 24, 1974

Inventor(s) Andre Deschamps and George Faye

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 4, line 20, read --In other terms-- instead of "In order terms".

Column 10, line 10, read --of the initial F_1 material-- instead of "of the initial I_1 material".

Signed and sealed this 1st day of April 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

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