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SQUARE LOOP FERROMAGNETIC MATERIAL

Filed Oct. 28, 1954

2 Sheets-Sheet 1

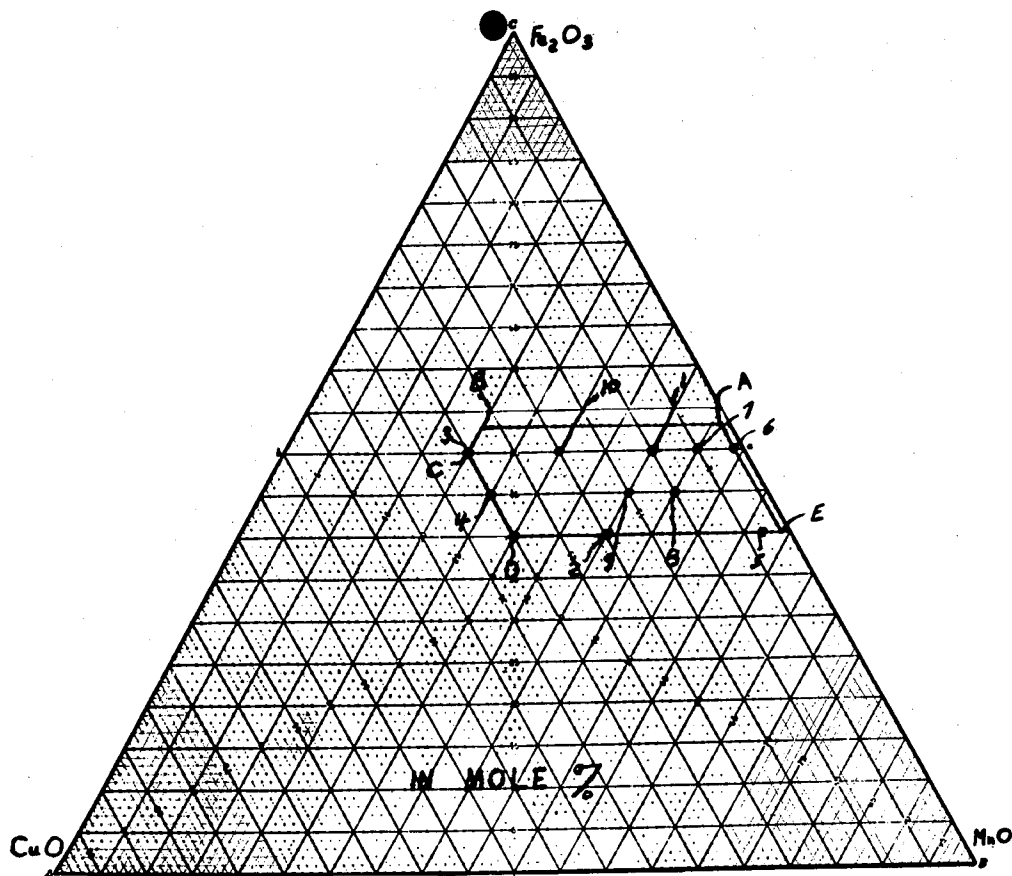


fig. 1

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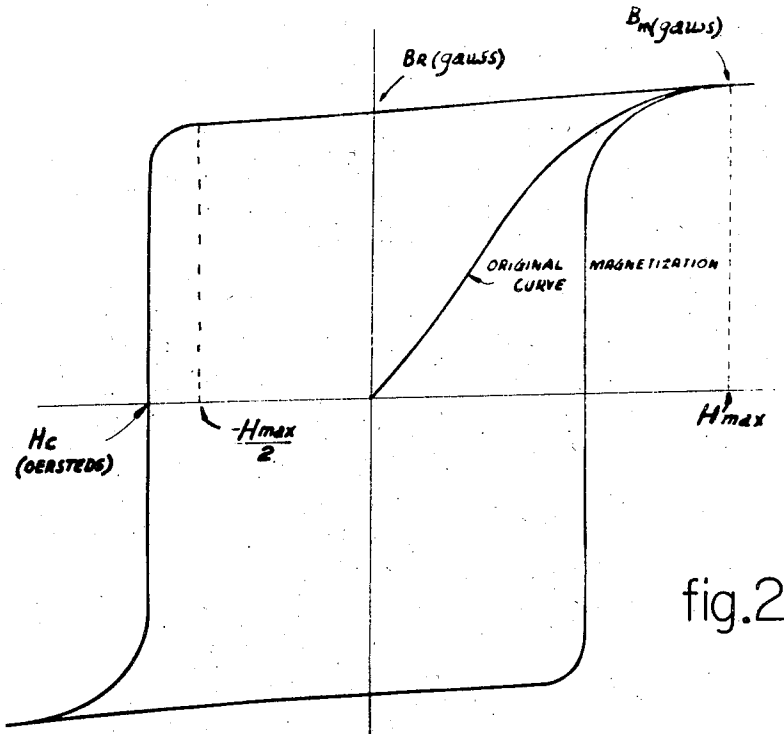


fig.2

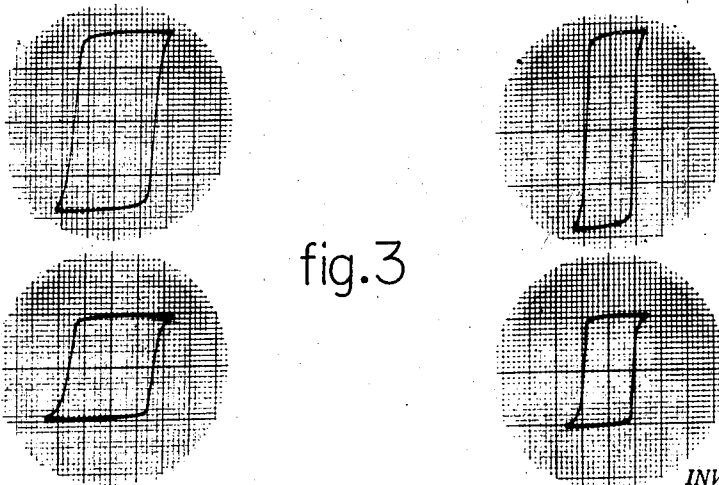


fig.3

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SQUARE LOOP FERROMAGNETIC MATERIAL

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8 Claims. (Cl. 252—62.5)

This invention relates to ferromagnetic materials and more particularly to ferromagnetic materials exhibiting hysteresis loops of substantially square configuration which are especially useful for computer and other magnetic memory applications.

Of recent years, the scope of the computer industry and other systems using memory devices has expanded enormously. With this expansion, there developed the need for more refined components necessitating materials of hitherto unrealized properties.

It is a principal object of this invention to provide non-metallic ferromagnetic materials which have substantially square hysteresis loops.

It is a further object of this invention to provide non-metallic ferromagnetic materials having a squareness ratio of about 0.7 and higher at large values of B_r and small values of H_c .

It is still a further object of the invention to produce non-metallic ferromagnetic components for memory circuit applications possessing improved characteristics enabling their use at much higher frequencies.

These and other objects of the invention will be best understood from the following description.

The present invention encompasses only ferromagnetic materials of the copper oxide-manganese oxide-iron oxide ternary system. We have found that certain copper oxide-manganese oxide-iron oxide compositions provide a ferromagnetic material exhibiting a substantially square hysteresis loop. In particular, we have found that the fired reaction product of a mixture of between about 40 and 53 mol percent of ferric oxide, between about 1 and 30 mol percent cupric oxide, and between about 20 and 60 mol percent of manganous oxide provides non-metallic ferromagnetic materials enabling the obtention of the desired results.

In accordance with a preferred feature of the invention, materials exhibiting the highest squareness ratio and the best high frequency behavior have been found to be characterized by a composition approximately corresponding to that of ferromagnetic ferrite materials, namely, a composition wherein the iron, expressed as Fe_2O_3 , constitutes 45 to 50 mol percent, and the copper, expressed as CuO , and manganese, expressed as MnO , range, respectively, between 5 and 20 and 35 and 50 mol percent of the mixture. Ordinarily, ferrite materials are characterized by the formula MF_2O_4 , wherein M represents one or more bivalent metals. However, since there is some uncertainty regarding the oxygen balance in the finished product of the invention, it has been impossible to generally characterize that product as a ferrite material. It is believed that for the stoichiometric composition as dictated by the above formula, a ferrite material is actually produced; however, where there has been a departure from stoichiometry, it has been impossible to ascertain whether or not the oxygen balance needed to produce the ferrite material has been maintained. Hence, for purposes of clarity, the composition of the invention has been defined in terms of the starting constituents.

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The invention will now be described in connection with the accompanying drawing wherein:

Fig. 1 is a ternary diagram of a copper oxide-manganese oxide-iron oxide system illustrating the composition of the materials of the invention. In this diagram, the copper oxide is expressed as cupric oxide, the manganese oxide as manganous oxide and the iron oxide as ferric oxide, all in mole percent;

Fig. 2 is a schematic hysteresis loop of a material of the invention;

Fig. 3 is an actual photograph of hysteresis loops obtained on an oscilloscope with materials of the invention subject to a 60 cycle per second alternating field illustrating the excellent squareness attained.

Referring now to the drawing, Fig. 1 illustrates a ternary diagram of the copper-, manganese-, iron-oxide system. As will be noted, the upper corner designates 100 mol percent of iron oxide, the lower left-hand corner 100 mol percent cupric oxide, and the lower right-hand corner 100 mol percent manganous oxide. The closed polygon ABCDE encompasses an area on the diagram substantially covering the compositions within the purview of the invention. Each of the points on the diagram within the polygon represents an actual composition in terms of starting constituents, from which a ferromagnetic material of the invention was produced. All of the materials were made in the following manner. A mixture of powdered ferric oxide, manganous carbonate and cupric oxide in proportions providing the desired composition in terms of mol percent, the manganous carbonate, in the course of the processing, being converted to the oxide, was thoroughly and intimately mixed in a high speed mixer and then prefired in air at about 1000° C. for about 60 minutes. The prefired mixture was then ball milled, filtered and dried.

A body of the desired shape and dimensions, usually a toroid, was formed from the dried powder by adding a small amount of water and pressing in a die at about 15,000 p. s. i. The body was thereafter fired in air or nitrogen at temperatures ranging from about 1100–1400° C. for between about one and four hours. The compositions thus prepared are illustrated on the diagram of Fig. 1 by reference numbers designating the composition and conditions of preparation as described in the following table:

Table I

Sample	Starting Composition, Mol Percent			Firing Conditions		
	Fe_2O_3	CuO	MnO	Atmos.	Temp., ° C.	Time, hrs.
1	50	10	40	N_2	1,300	1
2	40	20	40	Air	1,250	1
3	50	30	20	Air	1,150	1
4	45	30	25	Air	1,100	1
5	40	03	57	Air	1,300	1
6	50	01	49	N_2	1,350	1
7	50	05	45	N_2	1,300	1
8	45	10	45	N_2	1,350	1
9	45	15	40	Air	1,300	1
10	50	20	30	Air	1,250	1

Fig. 2 of the drawing illustrates a typical hysteresis loop for a material of the invention. The squareness ratio α , as a figure of merit for such materials, has been defined as the quotient of magnetic flux at minus one-half the maximum applied field producing the hysteresis loop

$$\left[B \left(-\frac{H_m}{2} \right) \right]$$

and the flux at said maximum applied field [$B_m(H_m)$]. That is to say,

$$\alpha = \frac{B\left(\frac{H_m}{2}\right)}{B(H_m)}$$

where H_m represents the maximum applied field. These values of the flux have been designated on the drawing. B_r and H_c represent the usual remanence and coercive force of the ferromagnetic materials. The ratio B_r/B_m is sometimes employed to also define squareness of the loop.

The magnetic properties exhibited by the samples whose composition and preparation are described in Table I are enumerated below:

Table II

Sample	H_m Oersted	B_m Gauss	B_r Gauss	H_c Oersted	α
1.-----	1.0	1,740	1,697	0.67	.90
2.-----	1.4	1,410	1,360	1.06	.82
3.-----	3.5	1,835	1,725	2.35	.74
4.-----	5.5	1,750	1,640	3.4	.71
5.-----	0.5	1,700	645	0.38	.70
6.-----	0.7	1,905	1,830	0.44	.80
7.-----	0.8	1,900	1,845	0.52	.89
8.-----	1.0	1,965	1,930	0.66	.89
9.-----	1.1	1,455	1,425	0.77	.87
10.-----	1.0	1,040	975	0.71	.78

As will be evident from Table II, essentially all of the materials of the invention exhibit a squareness ratio α of about 0.7 or higher, whereas the preferred compositions, i. e. those having an iron oxide composition of between 45 and 50 mol percent exhibit squareness ratios of about 0.85 or more.

The method of preparation of the materials of the invention will now be described in greater detail. The mixing, prefiring, filtering and drying steps are not particularly critical to the invention. Actually, they serve primarily to prepare the powdered oxides for the final sintering step during which the reaction occurs leading to the formation of the ferromagnetic materials of the invention. The above likewise applies to the pressing step. The pressure serves only to provide a coherent body to facilitate subsequent handling. In other words, varying the pressing force within reasonable limits will have little if any effect on the resultant magnetic properties exhibited by the completed components.

As is generally the case in the ceramic art, the important steps as regards the preparation of the materials are the sintering temperature and atmosphere, and sintering time to a lesser extent. In general, for an average-size toroid body having an O. D. of about 3 cms., an I. D. of about 2.2 cms. and a height of about 0.5 cms., sintering temperatures between about 1100 and 1400° C. for between about one and four hours are satisfactory.

As far as the atmosphere is concerned, satisfactory results have been obtained with air and inert atmospheres such as nitrogen. In general, strongly oxidizing and reducing atmospheres should be avoided. A nitrogen atmosphere is preferred for the smaller core bodies.

The ferromagnetic materials prepared in accordance with the invention all exhibit very high squareness ratios, which means that a change in polarization results in a very large output signal when such materials are employed in memory devices. These materials are further characterized by low values of H_c which enables moderate current pulses to initiate the change in polarization state of the material. Still a further advantage of our materials is the high magnetic induction, i. e., B_m , further en-

hancing the output signal level upon a change in polarization state.

In addition to memory devices and computer systems, the material of the invention is also useful in magnetic amplifiers.

While we have described our invention in connection with specific embodiments and applications, other modifications thereof will be readily apparent to those skilled in this art without departing from the spirit and scope of the invention as defined in the appended claims.

What is claimed is:

1. A ferromagnetic material having a substantially rectangular hysteresis loop consisting essentially of the reaction product obtained by firing in an atmosphere containing not more oxygen than air and at a temperature of about 1100° C. to 1400° C. of a finely-divided mixture of between about 40 and 53 mol percent of Fe_2O_3 , between about 1 and 30 mol percent CuO, and between about 20 and 60 mol percent of MnO.
2. A ferromagnetic material having a substantially rectangular hysteresis loop consisting essentially of the reaction product obtained by firing in an atmosphere containing not more oxygen than air and at a temperature of about 1100° C. to 1400° C. of a finely-divided mixture of about 45 to 50 mol percent of Fe_2O_3 , between about 5 and 20 mol percent CuO and between about 35 and 50 mol percent of MnO.
3. A ferromagnetic material having a substantially rectangular hysteresis loop consisting essentially of the reaction product obtained by firing in an atmosphere containing not more oxygen than air and at a temperature of about 1100° C. to 1400° C. of a finely-divided mixture of about 50 mol percent of Fe_2O_3 , about 10 mol percent CuO, and about 40 mol percent of MnO.
4. A ferromagnetic material having a substantially rectangular hysteresis loop consisting essentially of the reaction product obtained by firing in an atmosphere containing not more oxygen than air and at a temperature of about 1100° C. to 1400° C. of a finely-divided mixture of about 50 mol percent of Fe_2O_3 , about 5 mol percent CuO, and about 45 mol percent of MnO.
5. A ferromagnetic material having a substantially rectangular hysteresis loop consisting essentially of the reaction product obtained by firing in an atmosphere containing not more oxygen than air and at a temperature of about 1100° C. to 1400° C. of a finely-divided mixture of about 45 mol percent of Fe_2O_3 , about 10 mol percent CuO, and about 45 mol percent of MnO.
6. A method of making a ferromagnetic material comprising the steps of mixing in finely-divided form between about 45 and 50 mol percent of Fe_2O_3 between about 5 and 20 mol percent CuO and between about 35 and 50 mol percent of MnO, and subjecting the thus-formed mixture to an elevated temperature between 1100 and 1400° C. for about one to four hours in an atmosphere selected from the group consisting of air and nitrogen to form a ferromagnetic material exhibiting a substantially square hysteresis loop.
7. A method of making a ferromagnetic material comprising the steps of preparing a finely-divided mixture of oxides corresponding to a composition within the polygon ABCDE of the ternary diagram illustrated in Fig. 1 of the accompanying drawing, and subjecting the thus-formed composition to an elevated temperature between 1100 and 1400° C. in a non-reducing atmosphere containing not more oxygen than air for a time sufficient to form a ferromagnetic material exhibiting a substantially square hysteresis loop.
8. A method of making a ferromagnetic material comprising the steps of mixing in finely-divided form about 50 mol percent of Fe_2O_3 , about 10 mol percent CuO and about 40 mol percent of MnO, and subjecting the thus-formed mixture to an elevated temperature of about

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1300° C. in a nitrogen atmosphere for about one hour to form a ferromagnetic material exhibiting a substantially square hysteresis loop.

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