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3,197,412

FERRITE COMPOSITIONS

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2 Sheets-Sheet 1

FIG. 1

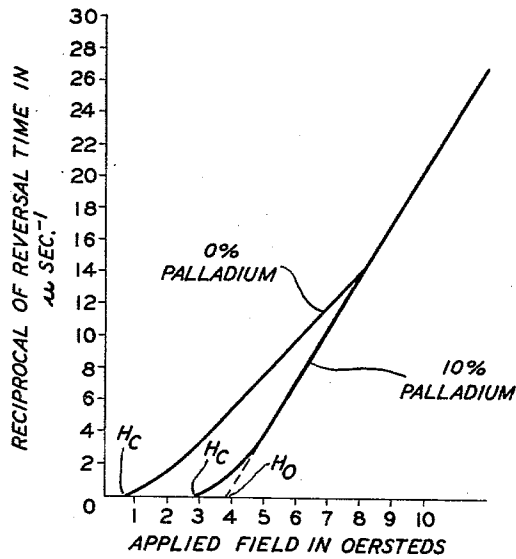
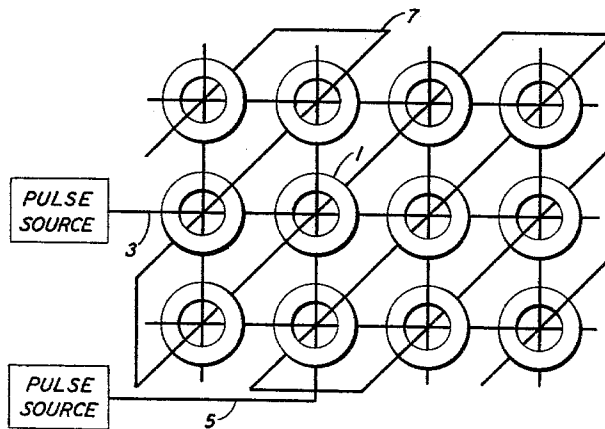


FIG. 2



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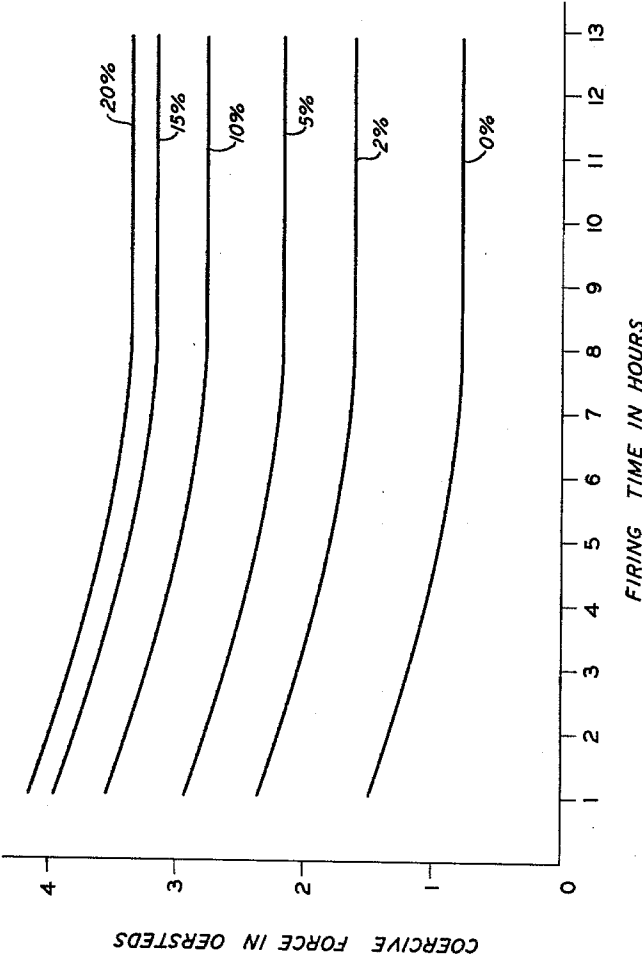


FIG. 3

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FERRITE COMPOSITIONS

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4 Claims. (Cl. 252-62.5)

This application is a continuation-in-part of United States application Serial No. 214,596, filed August 3, 1962 and now abandoned.

This invention relates to magnetic memory devices and, more particularly, to such devices in which information is stored in the form of representative magnetic states, to methods for fabricating materials used in such devices, and to the materials so produced.

Magnetic core memory devices, particularly those utilizing ferrite materials displaying a substantially rectangular hysteresis characteristic, are well known. Illustrative of such devices is the one described in an article by J. A. Rajchman in the October 1953 Proceedings of the Institute of Radio Engineers, volume 41, No. 10, pages 1407-1421, entitled "A Myriabit Magnetic Core Matrix Memory Element." The basic mode of operation of such memory structures involves wiring an array of cores such that any one core in the group can be magnetized independently of the others. Typically, this involves dividing the total magnetizing current required to magnetize or switch cores between two windings such that the one-half current in either winding alone is insufficient to switch the cores. However, the two half currents in both windings are large enough to magnetize or switch cores located at the intersection of the two windings. This provides the basis for setting each core in the array in the plus or minus state of magnetization to correspond to a binary code. The information is then read out by scanning the array with unidirectional half current pulses applied to the two windings and noting which cores give a flux reversal when subjected to both currents simultaneously.

An important consideration in devices of this type is that the magnetic flux reversal process associated with the coincident current selection technique desirably is accomplished with magnetic fields that approximate twice the coercive force (H_c) of the material. Providing ferrite materials having fast switching times at such fields is a prerequisite to satisfactory operation of such devices.

Commensurate with the knowledge of the art, a typical plot of the reciprocal of the switching time versus the applied field for conventional rectangular loop ferrites shows a nonlinear region having a relatively small slope occurring for fields substantially larger than H_c , and a sharply sloped linear region occurring at even larger fields. The extrapolation of the linear region to the field axis is called the threshold field H_0 for nonuniform rotation. The dominant flux reversal mechanism for fields below H_0 is the motion of the domain walls, while above H_0 it is nonuniform rotation. Because of the slope of the nonlinear region, the switching times associated with field values between H_c and H_0 are relatively long. The switching times associated with field values in the linear region of the curve above H_0 are, due to the slope, significantly shorter. Minimum switching times are obtained, therefore, for switching fields of $2H_c$ when H_c equals H_0 . Unfortunately, for the typical rectangular hysteresis loop ferrite compositions of the art, H_c is sufficiently less than H_0 so that the switching field of $2H_c$ falls within the nonlinear region on the plot.

In accordance with the present invention, it has been discovered that the inclusion of discrete particles of a second phase of palladium, platinum or thorium oxide in

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the matrix of rectangular hysteresis loop ferrite systems significantly lowers the switching times associated with the switching fields.

In particular, it has been determined that the presence of a second phase in such materials, while having little effect on the threshold value for rotational flux reversal (H_0), eliminates or sufficiently impedes domain wall motion so that the coercive force value H_c approximates the threshold value H_0 . As such, the switching fields ($2H_c$) associated with the materials of the invention permit fast switching times.

An important advantage accruing to the instant invention is that the ferrite compositions retain their excellent hysteresis characteristic, thereby assuring that the signal-to-noise ratio is maximized. Further, since a large number of rectangular hysteresis loop ferrite compositions are available to the art, each composition exhibiting its own particular threshold field, H_0 , the instant invention permits the attaining of a body having the particular coercive force and switching characteristic desired for the required use. For example, in many instances it is advantageous to utilize a coincident current memory device having a coercive force of about 0.1 oersted and a switching time of 3 μ sec., while other uses advantageously dictate bodies having a coercive force of about 5 oersteds and a switching time of .06 μ sec.

A more complete understanding of the invention may be gained from the following description in conjunction with the accompanying drawing, in which:

FIG. 1 is a graph on coordinates of reciprocal of reversal time in μ sec. against applied field in oersteds showing the switching speed of three samples of material: a magnesium-manganese ferrite containing 0 percent by weight palladium, or thoria, 32.1 mol percent MgO , 25 mol percent MnO , and 42.9 mol percent Fe_2O_3 ; a second sample of the same ferrite containing 10 percent by weight palladium; and a third sample of the same ferrite containing 4 percent by weight thorium oxide;

FIG. 2 is a plan view of a magnetic core memory device utilizing a ferrite core composition of the invention; and

FIG. 3 is a graph on coordinates of coercive force in oersteds against firing time in hours showing the effect of firing time during processing on the coercive force of five formed samples of a magnesium-manganese ferrite material, each sample containing 32.1 mol percent MgO , 25 mol percent MnO , 42.9 mol percent Fe_2O_3 , and varying amounts of palladium.

Referring more particularly to FIG. 1, the depicted graph illustrates the relationships between palladium inclusions and thorium oxide inclusions in typical rectangular hysteresis loop ferrite compositions and the switching times. As shown, the curves for the palladium and thorium oxide-containing compositions coincide. The improvement in switching times realized with palladium and thorium oxide additions is shown by a comparison of the palladium and thorium oxide-free ferrite composition with the identical compositions containing 10 percent by weight palladium and 4 percent by weight thorium oxide. As shown, palladium and thorium oxide inclusions in the ferrite compositions raise the coercive force, H_c , of the composition. At the same time, such additions have no effect on the threshold value, H_0 . This is evidenced by the coincidence of the upper portions of the two curves. In so minimizing the gap between the coercive force, H_c , and the threshold value, H_0 , the effect of the palladium and thorium oxide additions is to significantly shorten the switching time. Whereas the palladium and thorium oxide-free ferrite composition has a switching time of approximately 1.1 μ sec., the palladium-containing ferrite composition and the thorium oxide-containing ferrite composition have switching times of

only 0.013 μ sec. It has been determined that platinum inclusions give results comparable to palladium and thorium oxide inclusions.

The three samples depicted in FIG. 1 have the same basic ferrite composition: 32.1 mol percent magnesium oxide, 25 mol percent manganese oxide, and 42.9 mol percent ferric oxide. All samples were processed under identical conditions including a final firing at 1350° C. for ten hours.

The effect of varying the palladium concentration in ferrite compositions is illustrated in the following Table 1. In this table, there is set forth the coercive value, H_c , the terminal value, H_o , and the squareness value associated with zero percent, 10 percent, 12 percent, 15 percent, and 20 percent palladium inclusions in the same ferrite composition utilized in FIG. 1. Again, all samples were formed under identical processing conditions including a final firing of 1350° C. for ten hours.

Table 1

Percent Palladium	Squareness Ratio	H_c	H_o
0	0.97	0.8	4.2
2	0.94	1.7	4.4
10	0.94	2.8	4.5
15	0.94	3.2	4.7
20	0.90	3.4	4.6

As shown in Table 1, increasing palladium inclusions in the ferrite composition result in an increase in coercive force value, H_c . At the same time, the terminal value, H_o , remains substantially constant. It has been determined that platinum and thorium oxide give comparable results. Accordingly, Table 1, in conjunction with FIG. 1, establishes the enhanced switching times associated with palladium, platinum and thorium oxide additions to ferrite compositions. As further seen, increasingly larger additions adversely affect the squareness ratio. In view of these considerations, therefore, it is considered desirable to employ from one-half to 20 percent palladium, platinum or thorium oxide by weight of the total material in rectangular hysteresis loop ferrite compositions. Inclusions from 5 to 15 percent by weight are preferred. Amounts lower than one-half percent by weight do not sufficiently impede domain wall motion so as to significantly lower switching time, while inclusions larger than 20 percent by weight detract from the squareness of the hysteresis loop of the formed composition.

Although the ferrite composition used to illustrate the beneficial results of the palladium, platinum and thorium oxide additions of the instant invention was selected from the ferrite system defined by Albers-Schoenberg, United States Patent 2,715,109, issued August 9, 1955, the invention is not so limited. The previously described effect on switching time by such additions is equally applicable to other rectangular hysteresis loop manganese base ferrite compositions known to the art. Such compositions are defined by the art as having a Br:Bs value of at least 0.7 (United States Patent 2,818,387) and preferably at least 0.8 (United States Patent 2,981,689). The compositions further exhibit a maximum coercive force of 10 oersteds (United States Patent 2,882,236), with values as low as 0.1 oersted being realized for certain of the compositions (copending United States application Serial No. 213,639, filed July 31, 1962).

Commensurate with the art, the manganese base ferrite compositions may include additional oxide constituents for the purpose of adjusting the coercive force and squareness ratio characteristics to value considered desirable for the intended use. Exemplary of such constituents and conventional amounts thereof are: up to 55 mol percent magnesium oxide (United States Patent 2,981,689), up to 15 mol percent cadmium oxide (United States Patent 2,950,251), up to 30 mol percent copper oxide (United

States Patent 2,818,387), up to 9 mol percent nickel oxide (United States Patent 2,987,481), up to 18 mol percent zinc oxide (copending United States application Serial No. 213,639, filed July 31, 1962), up to 6 mol percent calcium oxide (United States Patent 2,981,689), up to 1.3 mol percent cobalt oxide (United States Patent 2,882,236), and up to 10 mol percent chromium oxide (United States Patent 2,950,252).

The use of such constituents to vary the coercive force and squareness ratio characteristics of manganese base ferrite compositions is well understood by the art and the formulation of any one desired manganese base ferrite composition is considered to be within the skill of the art and, accordingly, is not part of the instant invention. It is noted that such compositions typically have a ferric oxide content of about 25 to 50 mol percent and a manganese oxide content of about 4 to 67 mol percent. The amount of ferric oxide plus manganese oxide in such compositions is generally at least 45 mol percent, with a maximum amount for many of the compositions being 99 mol percent. The mol ratio of ferric oxide to manganese oxide is typically 0.37:1 to 12.5:1.

Although for ease of comparison all data detailed heretofore has been in terms of palladium and thorium oxide additions to ferrite compositions, the invention is not to be construed as being so limited. It has been determined that platinum is equivalent to palladium and thorium oxide for the purposes of the invention, and the exemplary data set forth in FIG. 1 and Table is equally applicable to platinum.

FIG. 2 depicts an illustrative magnetic core device utilizing palladium or platinum-containing ferrite cores of the invention. A complete description of the operation of this device is found in the aforementioned article by J. A. Rajchman. Briefly, by wiring the array of cores as shown, any core in the group, such as core 1, can be magnetized independently of the others by dividing the total magnetizing current equally between the two windings, 3 and 5. If properly chosen, the one-half current in either winding 3 or 5 alone would be insufficient to magnetize or reverse core 1, but the two half currents in the windings 3 and 5 will be large enough to magnetize or switch cores located at the intersection of the two windings, such as core 1. This provides the basis for setting each core in the array in a plus or a minus state of magnetization to correspond to a binary code. The information can be read out by scanning the array with unidirectional half current pulses applied to the horizontal and vertical windings 3 and 5 in a proper time sequence and noting which cores give a flux reversal when subjected to both currents simultaneously. The flux charge is detected through the readout winding 7, which can be common to all cores.

The magnetic memory device depicted in FIG. 2 is intended to be exemplary of an important use of palladium, platinum or thorium oxide-containing ferrite compositions. It is to be understood that such compositions, however, may be used in magnetic memory elements based on principles of operation different than those of the structure of FIG. 2.

The graph of FIG. 3 shows coercive force in oersteds as a function of firing times utilized during processing of five magnesium-manganese ferrite compositions. Each sample utilized the same basic ferrite composition set forth in conjunction with FIG. 1 and additionally contained varying amounts of palladium. The samples were prepared under identical processing conditions and utilized a firing temperature of 1350° C. in conjunction with the varying firing times shown in the figure. A comparison of the palladium-free ferrite composition with the 2, 5, 10, 15 and 20 percent palladium-containing compositions shows that such additions do not render the coercive force of the formed composition vulnerable to variations in firing times over the extended range of 7½ hours to 12½ hours. This range encompasses the firing times

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typically utilized in conventional ferrite-forming processes and, as seen, corresponds to that associated with the depicted palladium-free ferrite composition. Platinum and thorium oxide-containing compositions are equally invulnerable to variations in firing times.

The conventional ferrite-forming processes known to the art are suitable for forming the palladium, platinum or thorium oxide-containing ferrite compositions of the invention. During such processing, palladium, platinum or thorium oxide is added in particle form, either to the initial mixture of desired ingredients or during the subsequent ball-milling step. Preferably, the particles of palladium, platinum or thorium oxide have a particle size in the approximate range of 500 A. to 10,000 A. It has been found the smaller particles appear to have little deterrent effect on domain wall motion while larger particles act as nuclei for the walls and encourage wall motion at field strengths below H_c . Both effects detract from the enhanced switching times realized by the palladium, platinum or thorium additions in the invention.

The following specific example is given by way of illustration and is not to be construed as limiting in any way the scope and spirit of the invention.

Example I

Five initial mixtures were prepared containing 43.5 grams magnesium carbonate, 46.2 grams manganese carbonate, 110.3 grams ferric oxide and 0, 2, 10, 15, and 20 percent by weight palladium, respectively. The palladium particles were 1500 A. size in their longest dimension. After the successive steps of dry mixing, wet mixing in water and drying by filtration, the resulting ceramic materials were calcined at 900° C. for 16 hours. The calcined materials were then ball-milled for a period of two hours in water and a binder of 10 percent "Halowax". After ball-milling, the water was removed and the mixture was granulated through a 20-mesh screen having a

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mesh size of 0.84 millimeter. After a vacuum-drying operation at 50° C. for two hours, the particles were formed into rings under a pressure of 50,000 pounds per square inch. The rings had an outside diameter of 210 mils and an inside diameter of 175 mils. The rings then underwent final firing at a temperature of 1350° C. for nine hours in an oxygen atmosphere, and were allowed to cool to room temperature in a nitrogen atmosphere. The formed rings exhibited the magnetic characteristics set forth in preceding Table 1.

What is claimed is:

1. A rectangular hysteresis loop ferrite composition consisting essentially of 25 to 50 mol percent ferric oxide, 4 to 67 mol percent manganese oxide, up to 55 mol percent magnesium oxide, up to 15 mol percent cadmium oxide, up to 30 mol percent copper oxide, up to 9 mol percent nickel oxide, up to 18 mol percent zinc oxide, up to 6 mol percent calcium oxide, up to 1.3 mol percent cobalt oxide, up to 10 mol percent chromium oxide, and from ½ to 20 percent by weight of composition of at least one material selected from the group consisting of palladium, platinum and thorium oxide.

2. The ferrite composition in accordance with claim 1 wherein said material is palladium present in an amount of from 5 to 15 percent by weight of composition.

3. The ferrite composition in accordance with claim 1 wherein said material is platinum present in an amount of from 5 to 15 percent by weight of composition.

4. The ferrite composition in accordance with claim 1 wherein said material is thorium oxide present in an amount of from 5 to 15 percent by weight of composition.

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MAURICE A. BRINDISI, *Primary Examiner*.