

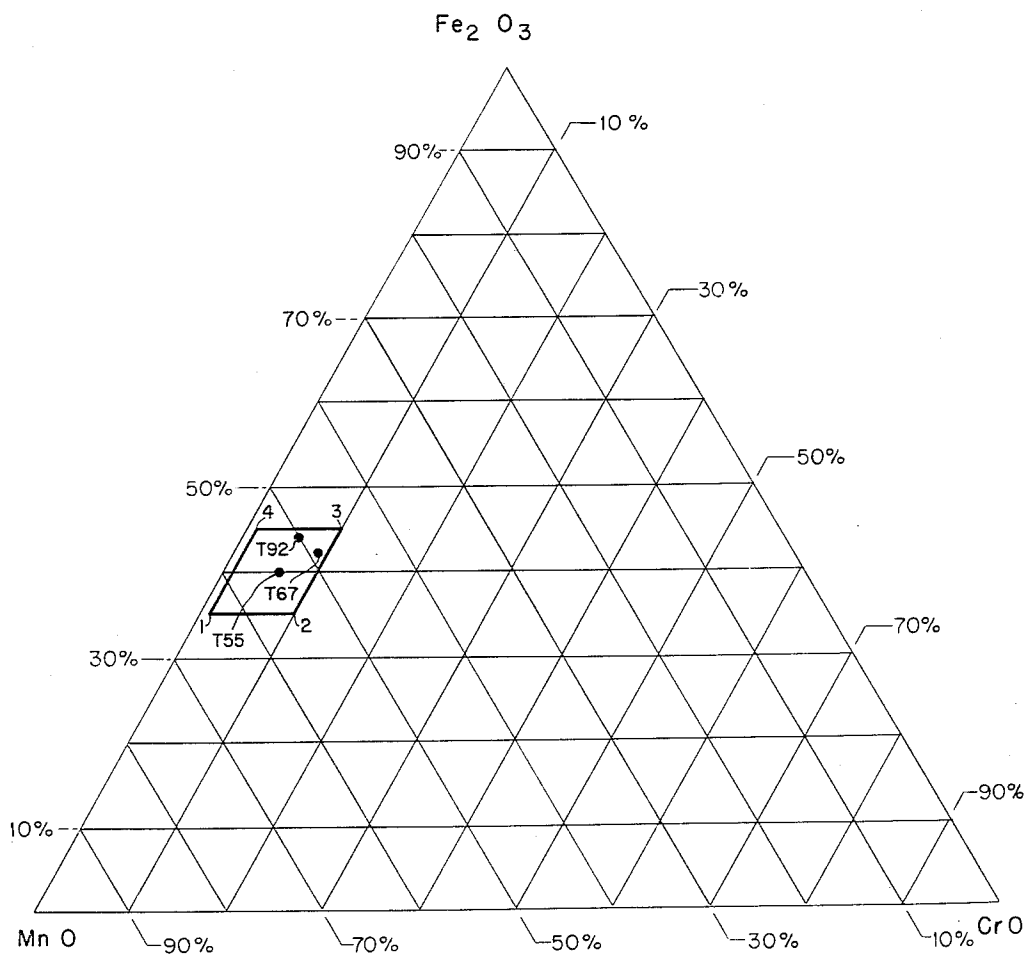
Aug. 23, 1960

J. M. BROWNLOW

2,950,252

MANGANESE CHROMIUM FERRITE COMPOSITION

Filed May 8, 1956



INVENTOR.
JAMES M. BROWNLOW

BY

William V. Schelberg
AGENT

1

2,950,252

MANGANESE CHROMIUM FERRITE
COMPOSITION

James M. Brownlow, Fishkill, N.Y., assignor to International Business Machines Corporation, New York, N.Y., a corporation of New York

Filed May 8, 1956, Ser. No. 583,539

5 Claims. (Cl. 252—62.5)

This invention relates to new ferromagnetic ceramic materials which have hysteresis characteristics of substantially rectangular shape, and to the production of bodies of such materials suitable for use as memory elements in digital information storage systems.

The composition comprises a mixture of manganese oxide, chromium oxide and iron oxide in the forming of a solid solution prepared from fine powders of certain oxides containing ions of these metals. Magnetic core elements are molded to a desired geometric shape after mechanical preparation of a mixture of desired relative proportions of the several oxides. Following the molding, the elements are subjected to suitable thermal treatment and crystallize in the cubic system known as spinels and generally known as ferrites.

Among the objects of this invention is to provide a ferromagnetic material which has a substantially rectangular hysteresis loop and high switching speed.

Another object of the invention is to provide a new and improved ferrite composition adapted for formation of memory elements useful in digital information storage systems.

These and other objects ancillary thereto are obtained by making a ceramic ferrite material consisting primarily of a manganese-chromium ferrite having a deficiency in trivalent iron as will be more clearly understood when explained in connection with the accompanying drawing in which the single figure is a triaxial diagram of the compositions in the system MnO, CrO, Fe₂O₃ plotted with mol percent ratios.

The ferrite series according to the present invention comprises a composition represented by the formula:



in which x, y and z represent the molecular percentages of the components. These percentages must lie within the following limits:

x=35 to 45 percent
y=45 to 60 percent
z=1 to 10 percent

The mixture percentages refer to the molecular proportions of manganese, chromium and iron oxides and accordingly are fixed regardless of the salt or particular oxide employed in the original mixture, as for example MnCO₃ or Cr₂O₃. In the final product formed after heat treatment or sintering the manganese oxide and the chromium oxide form the same substitutional solid solutions in ferrous ferrite, Fe₃O₄, notwithstanding the valence of the original manganese and chromium salt employed.

Applicant uses the following compounds in preparation of the initial mixture: ferric oxide Fe₂O₃, manganese carbonate MnCO₃ and chromic oxide Cr₂O₃. These materials are calcined at a temperature of approximately 1000° C. for a period of one to two hours and are thoroughly mixed so as to form a very homogenous mixture. This mixture is subsequently ground so that

2

the largest grain size is less than ten microns and a small percentage of lubricant material such as a monocrystalline wax or magnesium stearate and polyvinyl alcohol is added to reduce skin friction and warping during molding. The molding operation is performed by application of considerable pressure, and a fairly wide range of pressures may be used. The density of the body thus formed influences the grain size and magnetic characteristics, such as coercive force, of the final product and must be accurately controlled. In general, it may be said that the pressure of forming should be sufficient to provide a closely coherent body and should usually be greater than 40,000 pounds per square inch. A forming pressure of 50,000 pounds per square inch was used to mold a toroidal core having an I.D. of 0.0571 inch and an O.D. of 0.0888 inch.

The pressed body is in a so called green state and must be fired for an additional period of from ten minutes to several hours at temperatures from 1150° C. to 1440° C. in a non-reducing atmosphere, the longer period being required for the lower temperature range.

By way of example several groups of ferrites of the general manganese-chromium series are considered below that, while the properties may vary in accordance with different parameters of the process of manufacture such as temperature and cooling rate, have a ratio of remanence to saturation flux density of greater than 0.8 and a straight switching region of the B-H loop. These magnetic qualities are of importance in memory usage wherein binary information is represented by the states of remanence attained by such materials and short response times are desirable in changing from one remanence condition to the other.

Referring now to the single figure comprising a triaxial graph of the oxide system, hysteresis loops with a high B_r/B_s ratio are obtained for the following range of proportions as indicated within the lines connecting points 1, 2, 3 and 4.

	Mol percent
40 Fe ₂ O ₃	35-45
CrO	1-10
MnO	45-60

The following examples of specific compositions of the final product within these ranges are indicated with reference to points labeled on the diagram.

Table I

Sample	CrO	MnO	Fe ₂ O ₃	B _r /B _s
50 T55.....	6.0	54.0	40.0	0.9
T92.....	6.0	50.0	44.0	0.9
T67.....	9.0	49.2	42.8	0.8

Switching speeds for the compositions listed are in the order of two microseconds at fields of approximately two oersteds.

High residual to saturation ratios of flux density are obtained with the basic chromium-manganese ferrite with the addition of one or more bivalent oxide additives in a proportion of between 0 to 10 mol percent as indicated in Table II.

Table II (mol percent)

Sample	CrO	MnO ₂	Fe ₂ O ₃	CuO	MgO	NiO	CoO	B _r /B _s
65 K5.....	5.0	47.0	40.0	3.0	-----	5.0	-----	.90
T91.....	5.0	46.0	43.0	-----	6.0	-----	-----	.92
T89.....	6.0	49.0	40.0	-----	5.0	-----	-----	.92
T92.....	6.0	50.4	42.2	-----	-----	-----	1.4	.93

Switching speeds for the compositions listed in Table II are in the order of 1.8 microseconds at fields of approxi-

3

mately two oersted while the more ideal B_r/B_s ratios of over 0.9 are retained. The action of the additive oxides is not wholly understood but is believed not to be that associated with so called flux-materials and the addition of less than 10 mol percent is not considered to change the general character of the ferrite from that of the basic chromium manganese series.

It should be understood also, that the method of preparation of formed bodies may be varied greatly from that described without departing from the spirit of the invention. For example a large number of binder materials may be used, and the maturing temperature may vary over wide limits but is generally preferred between 1150° C. and 1440° C. Molding may be accomplished by any practicable method and extrusions are contemplated as a satisfactory mode of preparation of the green bodies of material.

It will be apparent from the foregoing description that the novel ferrite ferromagnetic composition set forth provides magnetic elements of superior characteristics useful in computers and otherwise for storage purposes, and that changes in amounts of constituents as well as conditions of treatment may be made without departing from the spirit of the invention as defined by the following claims.

What is claimed is:

1. A magnetic body exhibiting the characteristics of an essentially rectangular hysteresis loop and fast switching speeds at low driving fields consisting of the reaction product produced by heating together an intimate mixture of between 35-45 mol percent Fe_2O_3 , 45-60 mol percent MnO, and 1-10 mol percent CrO in a non-reducing atmosphere at a temperature within the range of 1150-1440° C.

2. A magnetic body exhibiting the characteristics of an essentially rectangular hysteresis loop and fast switching speeds at low driving fields consisting of the reaction product produced by heating together an intimate mixture of between 35-45 mol percent Fe_2O_3 , 45-60 mol

4

percent MnO, 1-10 mol percent CrO, and 0.01-10 mol percent of the oxide of the metals selected from the group consisting of Cu, Mg, Ni and Co in a non-reducing atmosphere at a temperature within the range of 1150-1440° C.

3. A magnetic body consisting of the reaction product produced by heating together an intimate mixture of 40 mol percent Fe_2O_3 , 54 mol percent MnO and 6 mol percent CrO in a non-reducing atmosphere at a temperature within the range of 1150-1440° C.

4. A magnetic body consisting of the reaction product produced by heating together an intimate mixture of between 35-45 mol percent Fe_2O_3 , 45-60 mol percent MnO, 1-10 mol percent CrO, and 0.01-10 mol percent NiO in a non-reducing atmosphere at a temperature within the range of 1150-1440° C.

5. A magnetic body consisting of the reaction product produced by heating together an intimate mixture of 40 mol percent Fe_2O_3 , 47 mol percent MnO, 5 mol percent CrO, and 5 mol percent NiO and 3 mol percent CuO in a non-reducing atmosphere at a temperature within the range of 1150-1440° C.

References Cited in the file of this patent

UNITED STATES PATENTS

2,744,873 Piekarski May 8, 1956

FOREIGN PATENTS

524,097 Belgium Nov. 30, 1953
1,074,864 France Apr. 7, 1954
1,107,654 France Aug. 10, 1955
735,375 Great Britain Aug. 17, 1955

OTHER REFERENCES

Philips Research Reports, vol. 9, No. 6, December 1954, pages 438-442.

Gorter: Proceedings of the IRE, December 1955, page 1900.