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3,068,176

FERROMAGNETIC CHROMIUM OXIDES CONTAINING FLUORINE AND THEIR PREPARATION

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No Drawing. Filed Mar. 31, 1958, Ser. No. 724,811
9 Claims. (Cl. 252—62.5)

This invention relates to novel ferromagnetic materials and their preparation. More particularly, it relates to ferromagnetic, fluorine-modified chromium oxides and to a method for their preparation.

Ferromagnetic materials are employed in a variety of applications. For example, these materials are used in magnetic sound-recording tapes, drums and records, memory devices, microwave circuitry, and as magnetic cores, such as coil cores in electronic equipment. In some of these applications, especially those requiring magnetic materials of low loss characteristics at high frequencies, ferromagnetic oxides are normally more useful than ferromagnetic metals.

Recently several forms of ferromagnetic chromium oxide having a tetragonal crystal structure have been prepared. These earlier materials include products modified with various elements which take positions in the crystal lattice normally occupied by chromium, but no substitution for oxygen has heretofore been disclosed.

We have now found that chromium oxides having desirable combinations of magnetic properties are produced by the introduction of fluorine atoms into the structure. Our novel and useful products are ferromagnetic chromium oxides having a tetragonal crystal structure and containing 48.0 to 61.8% by weight chromium and from about 0.1 to 5.0% by weight fluorine as an integral part of the crystal lattice.

Since the monovalent fluoride ion occupies a position usually occupied by the divalent oxygen ion, a concomitant change in valency of positive ions in the lattice is required to maintain electrical neutrality. This requirement can be met by the presence of chromium ions having a valency below 4 or by the complete absence of chromium atoms from an equivalent number of lattice positions yielding an electrically neutral, chromium deficient structure. Alternatively, positive lower valent foreign ions can be introduced in amounts stoichiometrically equivalent to the fluoride ions. This can be conveniently accomplished by introducing the fluoride ions and the positive lower valent foreign ions in the form of a metal fluoride. Metal fluorides having a tetragonal crystal structure of the rutile-type are especially suitable and constitute a preferred class of metal fluorides for use in this invention.

In its preferred embodiment, this invention provides novel and useful products which are ferromagnetic chromium oxides having a tetragonal crystal structure and containing 54.0 to 61.8% by weight chromium and 0.2 to 12.0% by weight of at least one metal fluoride having a rutile-type structure, i.e., the difluorides of manganese, iron, cobalt, nickel, magnesium, zinc, and palladium, as an integral part of the crystal structure. In other words, the metal of the rutile-type metal fluoride occupies spaces in the crystal lattice normally occupied by chromium while the fluorine atoms take positions normally occu-

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ried by oxygen. The metal atoms of the rutile-type metal fluoride may occupy positions adjacent or non-adjacent to positions occupied by the fluorine atoms. Products containing 58.0 to 61.8% by weight chromium and 0.2 to 6.0% by weight of a rutile-type metal fluoride exhibit higher saturation values than more highly modified products and constitute a particularly desirable class of fluoride-modified ferromagnetic chromium oxides in applications where high saturation values are especially important.

The ferromagnetic, fluoride-modified chromium oxides are produced in a form consisting essentially of tiny, irregularly shaped particles up to a few tenths of a micron across. They possess coercivities in the range of 20–100 oersteds and specific magnetizations or sigma values (σ_s) ranging up to 85 electromagnetic units per gram (emu./g.). Their Curie temperatures (T_c) range from about 80° C. to about 140° C.

It is noteworthy that the presence of fluorine in the crystal lattice lowers Curie temperature by as much as 50° C. When other modifiers are present also which, per se, increase Curie temperature, the net effect with respect to unmodified ferromagnetic chromium oxide may be either an increase or a decrease in Curie temperature. For example, the introduction of iron alone into the crystal lattice increases Curie temperature considerably, i.e., to 160° C. and above. However, the increase can be offset by the addition of fluorine and as shown in Example III which follows the Curie temperature observed for ferromagnetic chromium oxide modified with ferrous fluoride is about 135° C., i.e., only slightly above the Curie temperature of unmodified material. By varying the relative proportions of iron and fluorine, as for example by using mixtures of nickel fluoride and iron oxide, it is possible to obtain modified products having any desired Curie temperature between about 80° and about 160° C.

As indicated above, the fluoride-modified chromium oxides of this invention can be further modified if desired. In addition to iron, antimony is a particularly useful secondary modifier. Others include cobalt, nickel, manganese, vanadium, ruthenium, and the alkali metals. These modifiers, like the metals of the rutile-type metal fluorides, take positions in a crystal lattice usually occupied by chromium. For convenience, these modifiers are usually employed in the form of their oxides, but other compounds or the free elements may be used if desired. The amount of such secondary modifiers may vary from 0–14% by weight; it is preferred, however, that less than 7% of these modifiers be present. When a secondary modifier is employed, the chromium content of the resulting ferromagnetic chromium oxide may vary from 48.0 to 61.8% by weight.

The new fluorine-modified chromium oxides are prepared by heating chromium trioxide, CrO_3 , with a divalent metal fluoride having a crystal structure of the rutile-type, at a temperature within the range of 300–500° C. Although preformed metal fluorides are most convenient, combinations of other compounds which provide metal and fluorine in the proper ratio may be employed if desired. For example, the metal capable of forming a rutile-type fluoride may be introduced to the reaction in the form of oxide and hydrogen fluoride added as a co-reactant.

The reaction can be carried out over a wide range of

pressures. Pressures ranging from 1 to 3000 atmospheres, or more, are operable. Pressures of 1 to 1000 atmospheres are especially useful while pressures of 500–800 atmospheres are preferred since their use favors the formation of high quality products. Lower pressures, i.e., 1–500 atmospheres, are desirable when temperatures of 300–350° C. are employed.

As indicated above, reaction temperatures can range from 300–500° C.; however, temperatures of 350–450° C. are preferred, especially when operating pressures in the range of 500–800 atmospheres are employed. When antimony compounds are present as secondary modifiers, lower temperatures, i.e., 300–350° C., are beneficial. Temperatures above 500° C. are undesirable since they cause decomposition of the ferromagnetic chromium oxides.

The reaction time is not critical and may range from 10 minutes or less to 3 hours or more at the reaction temperature of 300–500° C.

Water is usually employed as a reaction medium in an amount of about 0.05 to about 6.0 parts for each part of chromium trioxide. Preferably, an amount of water ranging from 15–125% of the weight of the chromium trioxide is used.

The preparation of the ferromagnetic fluoride-modified chromium oxides involves the formation of one molecular proportion of oxygen from each two molecular proportions of chromium trioxide employed and the products correspond approximately to chromium dioxide, CrO_2 , modified in the manner stated above. Since oxygen is liberated, reaction vessels should be resistant to oxygen as well as to the other reactants. Materials of construction which may be used include platinum and the alloy known commercially as "Hastelloy" C.

The presence of fluoride ion in the crystal lattice of the products of this invention is indicated by the decreased Curie temperatures and by the inability to recover the modifiers from the products by washing, magnetic separation, or by other methods. Examination of the products by X-ray diffraction shows them to possess a tetragonal crystal structure of the rutile-type, i.e., of the same type as rutile, TiO_2 .

The ferromagnetic, fluoride-modified chromium oxides exhibit several magnetic characteristics which make them especially valuable for use in various specific applications. These critical properties are the intrinsic coercive force, H_{ci} , the specific magnetization or sigma value (σ_s), and the Curie temperature (T_c).

The definition of the intrinsic coercive force is given in Special Technical Publication No. 85 of the American Society for Testing Materials, entitled "Symposium on Magnetic Testing" (1948), pp. 191–198. The values for the intrinsic coercive force given herein are determined on a D.C. ballistic-type apparatus which is a modified form of the apparatus described by Davis and Hartenheimer in the Review of Scientific Instruments 7, 147 (1936).

The sigma value, σ_s , is defined on pp. 7 and 8 of Bozorth's "Ferromagnetism," D. Van Nostrand Co., New York, 1951. This sigma value is equal to the intensity of magnetization, I_s , divided by the density, d , of the material. The sigma values given herein are determined on apparatus similar to that described by T. R. Bardell on pp. 226–228 of "Magnetic Materials in the Electric Industry," Philosophical Library, New York, 1955.

The Curie temperature is determined by observing the force exerted on a specimen by a non-uniform magnetic field at a series of temperatures. The temperature above which ferromagnetism disappears is the Curie temperature (see Bozorth, *ibid.*, p. 6).

The invention is illustrated further by the following examples in which the proportions of ingredients are expressed in parts by weight unless otherwise noted.

EXAMPLE I

Two and five-tenths parts of commercial grade chromium trioxide, 0.06 part of manganous fluoride, and 0.41 part of water are placed in a flexible-walled platinum tube which is then hermetically sealed. The tube is placed in a pressure vessel capable of withstanding high pressures and a pressure of helium (water or another inert fluid may be employed if desired) amounting to 700 atmospheres is applied. The vessel is heated to 400° C., the pressure being vented from time to time so that a value of 800 atmospheres is not exceeded. A temperature of 397–402° C. and a pressure of 700–775 atmospheres are maintained for 3 hours. At the end of the reaction period, the vessel is cooled to about room temperature and the pressure carefully released. The platinum tube is removed from the pressure vessel and opened. The contents are washed with three changes of distilled water (which may be heated to boiling if desired), air dried, and finally dried more thoroughly in vacuum at a temperature in the range of 100–150° C. The product is a dark gray, strongly magnetic, modified chromium oxide having the following properties: intrinsic coercivity, H_{ci} , 36 oersteds; specific magnetization, σ_s , 63.6 emu./g.; Curie temperature, T_c , 109° C. Examination by X-ray diffraction shows the product to possess a tetragonal crystal structure of the rutile type. Chemical analysis gives the following results: Cr, 58.63; Mn, 1.36; F, 0.92.

EXAMPLES II–VI

The modification of ferromagnetic chromium oxide with various rutile-type metal fluorides is illustrated by Examples II–VI, summarized in Table I. The general procedure of Example I is followed with specific variations noted in this Table. Water (16% by weight based on total reactants) is employed as medium. In calculating the quantity of water to be used, allowance is made for water of hydration introduced with the reactants. The reaction conditions of 400° C. and 725 atmospheres pressure are maintained for 3 hours with a maximum variation of $\pm 5^\circ$ C. and ± 55 atmospheres. The properties of the resulting modified ferromagnetic chromium oxides are also summarized in Table I.

Table I

CHROMIUM TRIOXIDE HEATED WITH RUTILE-TYPE METAL FLUORIDES

Example No.	Modifiers, percent ^a	Magnetic Properties of Product		
		H_{ci} (Oersteds)	σ_s (emu./g.)	T_c (° C.)
II.....	FeF_2 , 2.4.....	b 51	79.4	136
III.....	CoF_2 hydrate, ^d 3.4.....	b 37	78.4	113
IV.....	ZnF_2 , 2.8.....	39	65.9	124
V.....	NiF_2 hydrate, ^d 4.3.....	40	62.6	^c 124
VI.....	MgF_2 , 1.0.....	38	76.5	124

^a Percent modifier based on weight of CrO_3 .

^b X-ray diffraction analysis shows these products to possess a rutile-type tetragonal crystal structure.

^c A nickel fluoride modified product prepared using 18.8% NiF_2 hydrate based on CrO_3 had a Curie point (T_c) of 80° C.

^d Analysis indicates 40.2% water in the NiF_2 hydrate, 37.3% water in the CoF_2 hydrate.

EXAMPLES VII–XI

Modification of ferromagnetic chromium oxide with a combination of a rutile-type fluoride and a metal oxide is illustrated by Examples VII–XI summarized in Table II. The general procedure of Example I is followed using the proportions of modifying metal fluorides and oxides shown in the Table. Reaction conditions of 400° C. $\pm 5^\circ$ C. and 750 ± 50 atmospheres for 3 hours are employed. The properties of the resulting modified chromium oxides are also listed in the Table. The reactions are carried out in the presence of 16% (based on weight of the reactants) water, due allowance being made for water introduced by the use of hydrated reactants.

Table II

CHROMIUM TRIOXIDE HEATED WITH RUTILE-TYPE METAL FLUORIDES AND A METAL OXIDE

Example No.	Modifiers, Percent ^a		Magnetic Properties of Product		
	Fluoride	Oxide	H _{ci} (Oerstedes)	σ_s (emu./g.)	T _c (° C.)
VII	MnF ₂ , 5.2	Sb ₂ O ₃ , 8.0	57	28.5	87
VIII	MgF ₂ , 3.6	Sb ₂ O ₃ , 8.0	^b 98	41.7	110
IX	NiF ₂ hydrate, ^d 4.3	Fe ₂ O ₃ , 2.9	65	65.5	140
X	CoF ₂ hydrate, ^d 3.5	Fe ₂ O ₃ , 2.0	^c 65	69.3	133
XI	MnF ₂ , 2.4	Fe ₂ O ₃ , 4.0 V ₂ O ₅ , 2.4	96	55.7	131

^a Percent modifier based on weight of Cr₂O₃.^b X-ray diffraction analysis shows this product to possess a rutile-type tetragonal crystal structure.^c Analysis of this product gave the following results: Cr, 55.29%; F, 1.02%; Co, 1.87%; Fe, 1.66%.^d Analysis indicates 40.2% water in NiF₂ hydrate, 37.3% in CoF₂ hydrate.

An important advantage of the products of this invention over hitherto known ferromagnetic chromium oxides lies in the greatly reduced Curie temperatures which they exhibit. These reduced Curie temperatures make the products useful in the fabrication of Curie point motors operating with relatively low-temperature sources of heat such as solar energy, and in magnetic switches used for example in fire alarm circuits.

Certain products of our invention, especially those containing antimony in addition to the rutile-type metal fluoride, exhibit a magnetic response which varies linearly with temperature, that is, the specific magnetization has a straight line relationship to temperature, over wide ranges of temperature. This novel property renders these products useful as the temperature sensing element in thermal regulators, recorders, and the like. Products having relatively low coercivities, i.e., below about 50 oersteds, are useful in the fabrication of memory and transformer cores. It is desirable in these applications that specific magnetization values be above about 40 emu./g.

The foregoing detailed description has been given for clearness of understanding only and no unnecessary limitations are to be understood therefrom. The invention is not limited to the exact details shown and described for obvious modifications will occur to those skilled in the art.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows. We claim:

1. A ferromagnetic chromium oxide having a tetragonal crystal structure and consisting essentially of 48.0 to 61.8% by weight chromium and 0.1 to 5.0% by weight fluorine as an integral part of the crystal structure.

2. A ferromagnetic chromium oxide having a tetragonal crystal structure and consisting essentially of 54.0 to 61.8% by weight chromium and as an integral part of the crystal structure 0.2 to 12.0% by weight of at least one metal fluoride having a rutile-type structure, the metal of said metal fluoride being selected from the group consisting of manganese, iron, cobalt, nickel, magnesium, zinc, and palladium.

3. A ferromagnetic chromium oxide of claim 2 in the form of tiny irregularly shaped particles.

4. A ferromagnetic chromium oxide having a tetragonal crystal structure and consisting of 48.0 to 61.8% by weight chromium, 0.2 to 12.0% by weight of a primary modifier comprising at least one metal difluoride, the metal of said metal difluoride being selected from the group consisting of manganese, iron, cobalt, nickel, magnesium, zinc and palladium, and as a secondary modifier from 0 to 14.0% by weight of an oxide of a member of the group consisting of iron, antimony, cobalt, nickel, manganese, vanadium, ruthenium, and alkali metals, the remainder of said ferromagnetic chromium oxide being oxygen.

5. Process for preparing a ferromagnetic, fluoride-modified chromium oxide having a tetragonal crystal structure and consisting essentially of 48.0 to 61.8% by weight chromium and 0.1 to 5.0% by weight fluorine as an integral part of the crystal structure, which comprises heating at a temperature within the range of from 300 to 500° C. and a pressure ranging from 1 to 3000 atmospheres, chromium trioxide with a divalent metal fluoride having a crystal structure of the rutile-type, the metal of said metal fluoride being selected from the group consisting of manganese, iron, cobalt, nickel, magnesium, zinc, and palladium, said chromium trioxide being present in an amount sufficient to produce a fluoride-modified chromium oxide of 48.0 to 61.8% by weight chromium, and said metal fluoride being present in an amount sufficient to produce a fluoride-modified chromium oxide of 0.2 to 12.0% by weight of metal fluoride.

6. Process for preparing a ferromagnetic, fluoride-modified chromium oxide having a tetragonal crystal structure and consisting essentially of 48.0 to 61.8% by weight chromium and 0.1 to 5.0% weight fluorine as an integral part of the crystal structure, which comprises heating at a temperature of from 300 to 500° C. and a pressure ranging from 1 to 3000 atmospheres chromium trioxide with hydrogen fluoride and an oxide of a metal of the group consisting of manganese, iron, cobalt, nickel, magnesium, zinc and palladium, whereupon a metal fluoride having a crystal structure of the rutile-type is produced in situ, said chromium trioxide being present in an amount sufficient to produce a fluoride-modified chromium oxide of 48.0 to 61.8% by weight chromium, and said hydrogen fluoride and said oxide of a metal being present in an amount sufficient to produce a fluoride-modified chromium oxide of 0.2 to 12.0% by weight of metal fluoride.

7. A ferromagnetic chromium oxide having a tetragonal crystal structure and consisting essentially of about 59.0% chromium, about 1.5% manganese, about 1.0% fluorine and the remainder oxygen, each of said percentages being by weight.

8. A ferromagnetic chromium oxide having a tetragonal crystal structure and consisting essentially of about 55% chromium, about 1% fluorine, about 1.5% cobalt, about 1.5% iron and the remainder oxygen, each of said percentages being by weight.

9. A ferromagnetic chromium oxide having a tetragonal crystal structure and consisting of 48.0 to 61.8% by weight chromium, as a primary modifier 0.1 to 5.0% by weight fluorine, and as a secondary modifier from 0 to 14.0% by weight of an oxide of a member of the group consisting of iron, antimony, cobalt, nickel, manganese, vanadium, ruthenium, and alkali metals, the remainder of said ferromagnetic chromium oxide being oxygen.

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