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MAGNETIC COMPOSITIONS CONTAINING IRON, RHODIUM, AND AT LEAST ONE MEMBER OF THE LANTHANIDE SERIES

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This invention relates to, and has as its principal object provision of, new magnetic materials useful for the interconversion and control of various forms of energy.

Magnetic materials, inclusive of both ferro- and ferrimagnetic materials, are broadly old and many such compositions are known. Similarly, many energy transducer devices based thereon are also known. However, the previously known ferromagnetic compositions suffered variously from one or more inferior properties, qualities, or behavior. For instance, many of the ferromagnetic compositions did not exhibit as high saturation magnetization values as was desired for many outlets, nor did they exhibit sufficient corrosion, oxidation, or high temperature resistance. While some of these ferro-, ferrimagnetic compositions did exhibit the rather peculiar property of an abrupt and large-scale increase in saturation magnetization with increasing temperature, those previously known either exhibited this so-called exchange inversion temperature at relatively low temperature and/or suffered from having too low a Curie temperature for successful application in many desired embodiments.

The iron/rhodium binary alloys of, for instance, Fallot, Revue Scientifique, 77, 498 (1939), and Kouvel et al., General Electric Research Report No. 61-RL-2870M, November 1961, also exhibited this abrupt increase in saturation magnetization with increasing temperature with a σ_{max} of about 112 gauss cm.$^{-3}$/g., i.e., 112 emu/g., as measured in a 5,000 oersteds (or conventionally a 5 koe.) magnetic field, but at a temperature of only 350° K. (i.e., about 77° C.). Furthermore, the temperature at which the material suddenly changes from antiferromagnetic to ferromagnetic could not be widely varied without increasing greatly the ratio of residual magnetization to maximum magnetization.

Recently there was discovered new and improved magnetic materials as disclosed and claimed in the copending coassigned applications of Walter, Ser. No. 177,230, filed March 5, 1962, and Ser. No. 177,229, filed March 5, 1962, based on metal alloys consisting essentially of iron and rhodium in major proportions and in minor proportion, respectively, at least one other member of the first long transition period of the Periodic Table of the elements of atomic numbers 21–30, inclusive, but exclusive of iron, and in the second application, again in minor amount, at least one other member of the second and third long transition periods of the Periodic Table of the elements of atomic numbers 39–48 and 57–80, inclusive, but exclusive of rhodium. These new ferromagnetic materials exhibit good saturation magnetization values and high Curie temperatures and at the same time are outstanding in corrosion and oxidation resistance, and thermal degradation.

There has now been discovered a new class of ferromagnetic materials which not only exhibit very good saturation magnetization values and high Curie temperatures but also exhibit higher saturation magnetization values at higher temperatures than the just referred to ferromagnetic materials of the said copending coassigned Walter applications. These compositions are also outstanding in corrosion and oxidation resistance and thermal degradation, properties in which many or most

of the presently known magnetic compositions are found wanting. They also exhibit very high hardness.

These superior magnetic compositions consist essentially of iron and rhodium in major proportion and at least one member of the lanthanum or lanthanide series of the Periodic Table of the elements of atomic numbers 58–71, inclusive, viz., cerium, praseodymium, neodymium, promethium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, and lutetium. The iron and rhodium will normally be present in substantially equal atomic proportions but not necessarily equal, since either may exceed the other by 20 atomic percent. It is, however, always necessary that both iron and rhodium be present. The at least one rare earth metal of the lanthanide series running from atomic number 58–71, inclusive, which also must always be present, will range in amount from 0.01 to 0.20 atom proportion. Thus, the new superior magnetic compositions of the present invention are alloys of the formula

$$Fe_aRh_b[xM]_c$$

wherein M represents a rare earth metal of the lanthanide series of atomic number from 58–71, inclusive; x is an integer from 1 to 14, and generally 1 to 3; a and b, which can be alike or different, are numbers ranging from 0.8–1.2; and c is a number ranging from 0.01–0.20 and in the instance when $x \geqq 2$, the requisite c's can be alike or different but still must fall in the indicated range. The subscript numbers a, b, and c refer to the atom proportions of the respective elements in the products. M can be different within the same defined group when x is greater than 1.

A particularly preferred subclass of these new magnetic materials exhibits a maximum saturation magnetization within a restricted temperature range and a very much smaller saturation magnetization at temperatures above and below this range. These preferred magnetic compositions exhibit a relatively low saturation magnetization at low temperatures which abruptly increases with increasing temperature, at a specific temperature range for each composition, to a maximum saturation magnetization many orders of magnitude greater than that exhibited at temperatures below this critical temperature range. This maximum saturation magnetization slowly decreases with increasing temperature until the Curie temperature is reached. On being cooled from the Curie temperature these preferred compositions exhibit slowly increasing magnetization with decreasing temperature until a maximum saturation magnetization value is reached and then abruptly exhibit a large decrease in saturation magnetization, reaching ultimately a low remanence saturation magnetization. The maximum saturation magnetization is generally the same on decreasing temperature as that achieved on increasing temperature. However, the temperature at which the maximum value is exhibited is somewhat lower on a decreasing temperature cycle than an increasing temperature cycle, i.e., there is magnetization hysteresis as a function of cycling temperature.

Not only is this subclass of the magnetic compositions of this invention preferred, but also devices for the interconversion and control of various forms of energy based on this preferred class of magnetic compositions comprise another preferred portion of the present invention. Another preferred embodiment of the invention is directed to methods for preparing these preferred magnetic products exhibiting these novel magnetic properties, and also to the preparation of energy transducers broadly based on such products.

The proportions of metals within the alloys of this invention can be expressed in somewhat different terminology as follows: iron, about 33.33–59.70 atom percent;

rhodium, about 33.33–59.70 atom percent; and at least one lanthanide of atomic number 58–71, about 20.0–0.415 atom percent. It is to be distinctly understood that at least one lanthanide of atomic number 58–71 is comprised within the designated 20.0–0.415 atom percent and that up to 14 of such elements can be present.

The following examples in which the parts given are by weight are submitted to illustrate the present invention further and not to limit it.

σ_{res} is used to indicate the residual saturation magnetization of the sample in emu/g. The symbol σ_{max} is used to indicate the maximum saturation magnetization of the material in emu/g., and the column headed temp-σ_{max} indicates the temperature at which this maximum saturation magnetization value is attained. In all instances in all columns involving temperature the units are in ° C. The saturation magnetization data were obtained using a magnetic field of 15.75–16.00 koe. (i.e., kiloersteds or 15,750–16,000 oersteds).

Table I

Composition	Anneal Time, hours	Heating T_s	Cooling T_s	Tc	σ_{res}	σ_{max}	Temp.-σ_{max}
Fe/Rh/0.0833 Gd	40			525		132.0	−195
Fe/Rh/0.0833 Tm	40	37		444	0.5	110.0	138
Fe/Rh/0.0833 Ho	40			528		127.3	−195
.8 Fe/1.2 Rh/.10 Er	28	96		440	3.8	45.8	127
1.2 Fe/.8 Rh/.20 Sm	28			728		118.4	−195
Fe/Rh/.05 Tb/.05 Nd	28			532		127.4	−195

EXAMPLE I

An intimate mixture of 2.9833 parts of iron and 5.4986 parts of rhodium, all in finely divided form was placed in a die and pressed into a pellet. The pellet was then placed in the water-cooled copper cup of a D.C. electric arc furnace. On top of the pellet was placed 0.6234 part of cerium metal in the form of a lump. The furnace was then sealed, flushed several times with purified argon, and finally filled with argon at a pressure of one atmosphere. An arc was struck and the metals fused together. In operating this arc, the copper was the positive electrode and thoriated tungsten was used as the negative electrode, and the voltage was 5–25 volts and the amperage was 50–150 amps. The current was shut off and the sample turned over. The arc was then restruck and the sample remelted. This turning and remelting process was repeated to a total of eight times to insure homogeneity. Following the final melting, the furnace was allowed to cool and the product was removed. The metallic product was slightly magnetic at room temperature.

To further homogenize the sample and to encourage ordering of the crystal lattice, the metal slug was sealed in an evacuated silica tube and heated to 950° C. for 40 hours, after which it was cooled slowly to room temperature over a period of 24 hours. After this annealing treatment, the slug appeared superficially unchanged. However, it was now almost non-magnetic at room temperature, exhibiting a residual magnetization of less than 2.0 emu/g. On heating to above 118° C. the magnetization increased rapidly to a maximum of 106.5 emu/g. at 159° C. On further heating the magnetization fell off to the Curie point of 445° C.

For brevity, the additional detailed examples illustrative of the present invention are covered in the following table in which these new magnetic compositions were prepared as described in full detail in Example I in the foregoing with the indicated variations in charge composition, annealing time, and the resultant different magnetic properties. As in Example I, in all instances the charge was arc-melted, turned, and remelted a total of eight times. In this table the charged compositions are in the indicated atomic proportions. The annealing time was, in all instances, at 950° C., and the symbol T_s refers to the temperature at which the indicated new magnetic composition undergoes the rapid and large-scale change in saturation magnetization. The column T_s (heating) lists the temperatures at which such a phenomenon occurs as the sample is raised from a lower temperature, and the column headed T_s (cooling) indicates the temperature at which the sample undergoes the abrupt large-scale decrease in saturation magnetization on cooling from a higher temperature. The symbol T_c is used to represent the Curie temperature. The symbol

Suitable specific compositions within the scope of the present invention, i.e., those materials consisting essentially of Fe, Rh, and at least one element of the lanthanide series of atomic number 58 through and inclusive of 71, include

$Fe_{1.0}/Rh_{1.0}/Ce_{0.2}$, $Fe_{0.95}/Rh_{1.08}/Pr_{0.05}$, $Fe_{1.1}/Rh_{1.1}/Nd_{0.2}$, $Fe_{0.9}/Rh_{1.1}/Pm_{0.1}$, $Fe_{0.8}/Rh_{1.2}/Sm_{0.1}$, $Fe_{0.9}/Rh_{1.0}/Eu_{0.01}$, $Fe_{0.9}/Rh_{1.0}/Gd_{0.1}$, $Fe_{1.2}/Rh_{0.8}/Tb_{0.05}$, $Fe_{1.0}/Rh_{1.1}/Dy_{0.05}$, $Fe_{1.0}/Rh_{0.9}/Ho_{0.15}$, $Fe_{1.0}/Rh_{1.2}/Er_{0.15}$, $Fe_{1.1}/Rh_{1.2}/Tm_{0.05}$, $Fe_{1.0}/Rh_{1.0}/Yb_{0.1}$, $Fe_{1.0}/Rh_{1.1}/Lu_{0.05}$,

and the like. As stated in the foregoing, the present invention is not limited compositionwise to three-component compositions similar to those just specifically named wherein there is present in the alloys Fe and Rh in major amount and a minor amount of a lanthanide but is also inclusive of those alloy compositions consisting essentially of Fe and Rh in major amount and relatively minor amounts of more than one lanthanide. Thus, the present invention is also specifically inclusive of four, five, six, seven, eight, etc., element-containing alloys wherein the Fe and Rh are always present and in major amount, and the other elements are present in minor amount and are all lanthanides. Thus, to be specific, the present invention also includes the following multicomponent magnetic alloys:

$Fe_{1.0}/Rh_{1.0}/Ce_{0.1}/Pr_{0.05}$, $Fe_{0.8}/Rh_{1.2}/Yb_{0.05}/Lu_{0.05}$,

$Fe_{1.2}/Rh_{0.9}/Ho_{0.02}/Er_{0.02}/Tm_{0.02}$,

$Fe_{0.9}/Rh_{1.2}/Tb_{0.05}/Dy_{0.05}$,

$Fe_{0.9}/Rh_{1.2}/Sm_{0.02}/Eu_{0.02}/Nd_{0.1}/Pm_{0.1}$,

$Fe_{0.9}/Rh_{1.9}/Ce_{0.2}/Er_{0.05}/Pr_{0.10}/Gd_{0.05}$,

$Fe_{1.1}/Rh_{1.2}/Ce_{0.05}/Pr_{0.05}/Sm_{0.02}/Gd_{0.02}/Tm_{0.02}/Yb_{0.02}/Lu_{0.01}$,

and the like. While varying modifying amounts of the lanthanides can be present in these new alloys which have Fe and Rh in major amount and two or more of the said lanthanides, generally speaking there will be a total of no more than 0.2 to 0.4 atom proportions of said other modifying transition elements in any one alloy.

The novel compositions of the present invention exhibit a maximum saturation magnetization at temperatures in the range −269° C. to +375° C. and Curie temperatures in the range +350° to +600° C. The preferred magnetic compositions also exhibit increasing saturation magnetization with increasing temperature in a temperature range below the Curie point.

Such compositions are useful in devices operating at temperatures near room temperature and even at elevated temperature for those exhibiting maximum saturation

magnetizations in the higher temperature ranges. Those exhibiting maximum saturation magnetization at very low temperatures are especially useful in devices such as refrigerators and temperature-sensitive controls operating at temperatures near the boiling point of liquid helium and below. The manner in which saturation magnetization varies with temperatures can be controlled by modifying the composition of the ferromagnetic products. The most outstanding compositions exhibit a very low residual magnetism below the lower ferromagnetic transition temperature.

These novel magnetic compositions are prepared by heating mixtures of the elements or compounds of the elements to a temperature in the range from 600 to 2500° C., or higher, as equipment and vapor pressure limitations dictate within the normal practice. Temperatures of 700 to 850° C. and from 1200 to 1700° C. are usually employed. Temperatures of at least about 1550–1600° C. are generally necessary if the compositions are to be melted, which is preferred, preferably in an arc. The time of heating is not critical but should be sufficient to permit complete reaction of the ingredients. Heating times ranging up to about 50 hours for the lower temperature ranges are necessary to effect appreciable solid state reaction. Longer times can be useful in some cases, particularly, for instance, if it is desired to prepare the composition in single crystal form. Generally speaking, the most efficient technique in the sense of obtaining the most complete reaction is to carry out the reaction in the melt for time periods of from at least 5 to about 60 minutes or longer. Most preferably the reaction is carried out in the melt in an arc furnace with repeated remelting and repositioning to assure homogeneity.

Heating can be carried out at amospheric pressure with the reactants protected by a blanket of inert gas such as helium or argon. Alternatively, the reaction can be conducted in an evacuated vessel. It is also possible to employ superatmospheric pressure. The reaction can also be carried out in sealed vessels under the autogenous pressure developed by the reaction mixture at the reaction temperatures. Since the preferred techniques involve effecting reaction in the melt, it is normally preferred to carry out the reaction in inert refractory materials under reduced pressure or under a protective blanket of an inert gas.

The materials employed in preparing these new compositions can be the elements themselves or any of the binary or ternary combinations thereof as called for by the desired stoichiometry. Thus, to prepare Fe/Rh/Ce the three elements themselves can be charged or the necessary Fe/Rh binary can be separately prepared previously and then mixed with the requisite amount of Ce and reaction effected to form the desired ternary composition. In any event, it is preferred that the materials be in powder or granular form and that they be well mixed before heating is commenced.

The starting materials are employed in such relative amounts that the resulting mixture contains the desired proportions of Fe/Rh and the requisite at least one lanthanide. Thus, to prepare an $Fe_{1.1}/Rh_{1.2}/Lu_{0.02}$ the respective elements or binaries are charged in the indicated relative atomic proportions.

After the desired preparative heating cycle has been completed, the reaction mixture is cooled and, if desired, subjected to purification, e.g., by extraction with acids or, after grinding, by magnetic separation. This first cooling cycle will be relatively rapid.

To assure the greatest homogeneity in the product and the maximum ferromagnetic behavior, it has been found that the products should preferably be annealed by holding for a relatively long time at an elevated temperature and then slowly cooling to room temperature over a controlled temperature profile, e.g., by a suitably programed recorder-driven furnace. Thus, it is preferred that the products of the present invention after the preparative heating ond cooling cycle, whether or not any intervening mechanical, chemical, or magnetic purification is effected, be heated to an elevated temperature in the range 800–1000° C. or higher and held at this temperature for relatively long periods of time, e.g., from 24 to 100 hours or so, in an inert atmosphere, i.e., under evacuated conditions or with a protective blanket of an inert gas such as argon or helium. Then, the compositions of the present invention are further annealed carefully by final slow cooling from this temperature to room temperature over a period of approximately 24 hours.

The novel magnetic compositions of this invention exhibit several magnetic characteristics which make them especially valuable for use in various specific applications. The novel lower ferromagnetic transition temperature is a distinguishing feature conferring unusual utility on these materials. Particularly outstanding are the relatively high saturation magnetization values exhibited by these compositions, as well as the high Curie temperature and good values of saturation magnetization exhibited at the maximum with increasing temperature below the Curie temperature. All the compositions are resistant to corrosion, oxidation, and exhibit good magnetic behavior at elevated temperatures.

The preferred products are useful in devices for the interconversion and control of various forms of energy such as solar motors, temperature-sensitive inductors, thermally activated clutches, and temperature compensators in devices based on conventional magnetic material where sagging of magnetic properties with increasing temperature is functionally deleterious. In their essential features all of these devices comprise at least three components, viz., the magnetic component described previously, suitable means for applying a form of energy to and from the magnetic component, and suitable means for utilizing the output from the magnetic component. For some applications, the devices of the present invention can include means for controllably magnetizing and demagnetizing the magnetic component. At temperatures within the ferromagnetic range, these compositions can be used in any of the conventional applications for ferromagnetic materials for which their properties render them suitable, e.g., electromagnets, high-frequency coil cores, information and memory storage elements, and the like.

In the preferred devices the elements which provide heat to or remove heat from the magnetic element, which magnetize and demagnetize the magnetic element, and which collect and detect the new form of energy produced are conventional in the art. For example, by introducing a pivotal element, with a magnetic component as just described, in a magnetic field and having means for magnetizing the magnetic component, the pivotal elment can be caused to move in said field. In this way, mechanical work can be done. The pivotal element can be an armature, an oscillating arm, or a metering device.

The preferred compositions of the present invention are useful as the active component in forming temperature responsive electrical inductors comprising, usually in combination, a metallic core consisting at least in part of one of the present magnetic compositions with or without a second material exhibiting a magnetic permeability which is substantially invariant with temperature, and an electrical conductor wrapped around said core. These temperature responsive electrical (magnetic) inductors are widely useful in any circuits in which inductance is a significant parameter. Thus, these inductors based on the present magnetic compositions can be employed as an element of the frequency-determining circuit of a sine-wave oscillator or as high-temperature safety device to reduce circuit current with increasing temperature or as a current-controlling device in which the control current flows through a heater wind-

ing on the temperature-sensitive inductor. In addition, these temperature-responsive inductors can be used in conjunction with a wide variety of conventional core materials, including both the metallic and oxide types, representative of which latter are, for example, the ferrites.

In view of the increasing saturation magnetization with increasing temperature below the Curie temperature, the preferred materials of the present invention are useful in forming temperature responsive magnetically operated rotary force couplings comprising in combination, a pair of relatively rotatable elements to be coupled disposed adajcent to one another in a common magnetic flux path, a permanent magnet, and one of the new magnetic compositions of the present invention which exhibits a changing permeability accompanying a reversible first order transition from a first solid state phase to a second solid state phase at a given temperature, both disposed in said common magnetic flux path, the permanent magnet and the magnetic composition of the present invention completing a magnetic flux circuit between the said elements of the pair coupling one of the elements with the other in that temperature range when the magentic composition of the present invention exists in a first solid state phase and uncoupling the elements of the pair as the temperature decreases when the substance exists in a second solid state phase, and obviously the reverse and in cycles.

The preferred compositions of the present invention are also useful in thermomagnetic devices as the working substance therein, said devices being useful for effecting heat transfer, i.e., serving as heat pumps, e.g., a refrigerator. These new magnetic compositions in such devices in view of the first order solid phase to solid phase transition with changing temperature with accompanying relatively large change in internal energy content in going through the transition will function as the said working substance in said devices with allied coupled magnetic means for cyclically inducing said transition in a direction such as to lower the temperature of the substance when one solid state phase is attained and to increase the temperature when the other solid state phase is attained, along with an allied heat source and a thermal sink relative to one of the solid state phases individually adapted to effect heat transfer sequentially with respect to said substance.

With respect to the thermomagnetic working capability of the preferred compositions, they are of particular interest in the formation of gradient objects comprising the said magnetic materials varying in composition angularly about a point or axis or varied along one or more selected lines, which need not be straight, in the said gradient object such as to display the first order solid phase to solid phase transition at successively higher temperatures in a first path or a direction along or about said point or axis of said line, and at successively lower temperatures in an opposite path or direction achieved by varying the composition of the magnetic alloys. These gradient objects are particularly useful in many kinds of energy-converting devices, e.g., as temperature indicators, cores in temperature-sensitive inductors, transformers, elements in thermal switches, and the like, and are particularly outstanding because of the possible ready and precise adjustment of device operation achievable to suit particular environmental conditions obtained with the great control possible through the narrow compositional changes.

These preferred materials are also useful as the working substance in a method of information storage and retrieval wherein a recording member containing one of the new magnetic compositions of this invention substantially homogeneously distributed therethrough is exposed to a read-in beam, modulated patternwise in accordance with information to be stored from a temperature variation inducing component, thereby establishing in the said recording member regions of relatively higher and relatively lower intrinsic magnetization corresponding to said information, maintaining said element after said read-in at a temperature within the thermal hysteresis range, and reading out the stored information by exposing the element at said temperature to a low intensity electron beam whereby deviations in said beam corresponding to the stored information are produced and converted into electrical signals. Intrinsic magnetization is used here as defined by Cusack, "The Electrical and Magnetic Properties of Solids," Longmans-Green & Company, London, 1958, page 315.

The first order solid phase to solid phase transition accompanied by thermal hysteresis which is exhibited by the preferred materials is characterized by abrupt change not only in the magnetic properties but also in a number of the other physical properties of the materials and any of these properties can be employed in any sensing or read-out method. Thus, after modulated read-in, read-out can be based on the change in electrical resistance of the new magnetic materials serving as the working substance of said recording member simply by providing read-out means sensitive to changes in resistance. Alternatively, read-out can be based upon changes in a linear dimension or in a volume of the working substance as desired.

Because of their outstanding magnetic properties coupled with good stability to temperature, atmosphere, corrosion, oxidation, and the like, and particularly because of the relatively high Curie temperatures that they possess, the preferred magnetic materials are broadly outstanding as the working substances in various devices whereby, generically, magnetic energy is changed controllably to mechanical, electrical, or thermal energies; mechanical energy is converted controllably into electrical, magnetical, or thermal energies; or thermal energy is controllably converted to mechanical magnetic, or electrical energies.

More specifically, the preferred compositions of the present invention can serve as the working substances in magnetic switches, radiation-intensity meters, reciprocating engines, devices for maintaining constant temperature difference between two zones, magnetic balances, thermomagnetic generators, solar motors, temperature indicators, image-forming components, magnetic flashers, variable resistors, differential transformers, temperature responsive resonators, and the like.

Since obvious modifications and equivalents in the invention will be evident to those skilled in the chemical arts, I propose to be bound solely by the appended claims.

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

1. An alloy composed of (A) iron, (B) rhodium, and (C) at least one lanthanide of atomic number 58–71 in the atom proportions of 0.8–1.2 of (A), 0.8–1.2 of (B) and 0.01–0.40 of (C).

2. An alloy of claim 1 in which (C) is cerium.

3. An alloy of claim 1 in which (C) is gadolinium.

4. An alloy of claim 1 in which (C) is holmium.

No references cited.