

Feb. 2, 1971

E. A. NESBITT ET AL

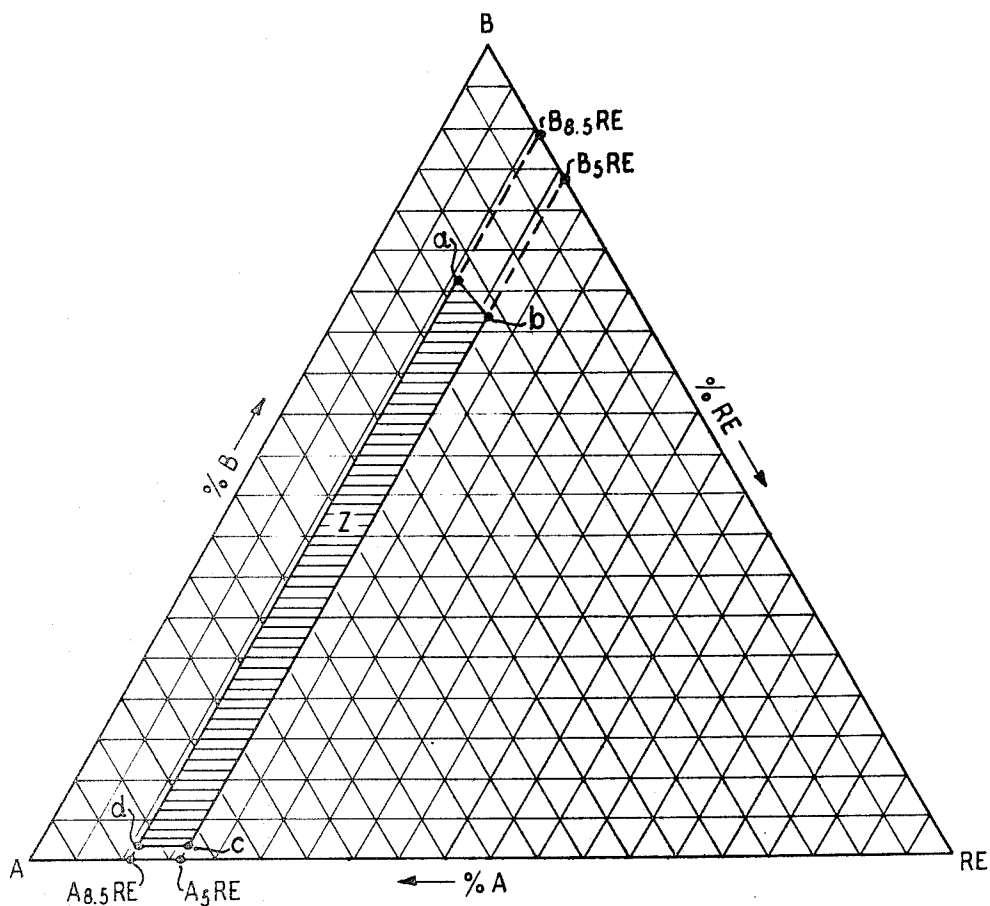
3,560,200

PERMANENT MAGNETIC MATERIALS

Filed April 1, 1968

3 Sheets-Sheet 1

FIG. 1



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FIG. 2

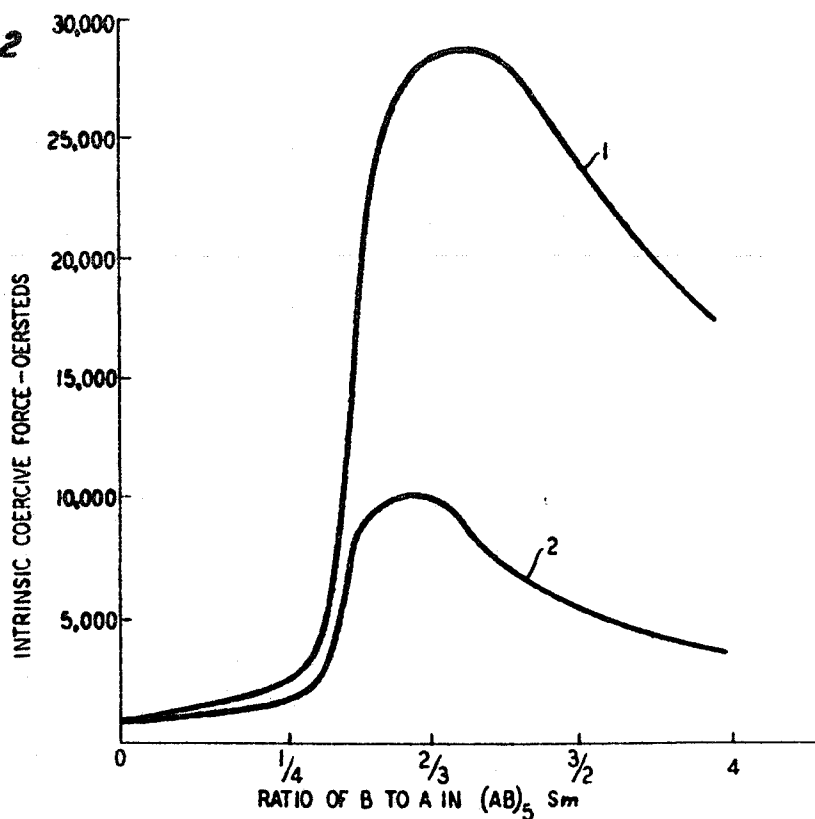
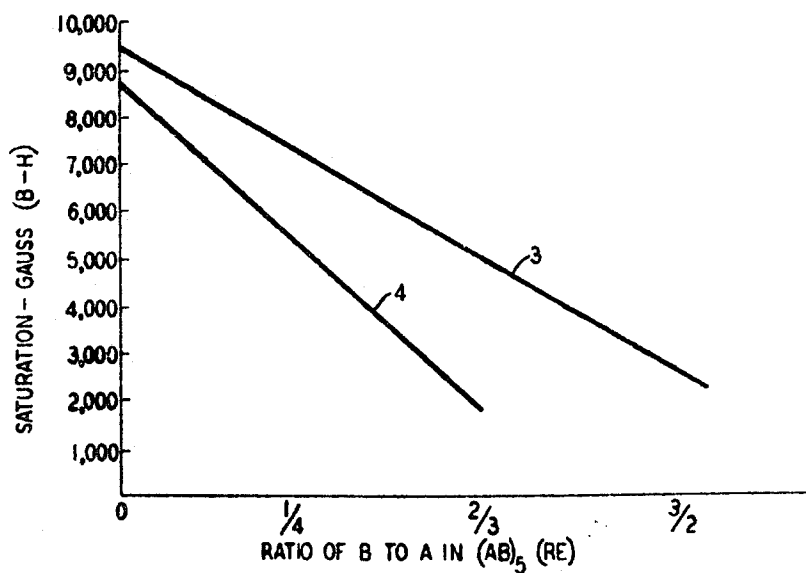


FIG. 3



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FIG. 4

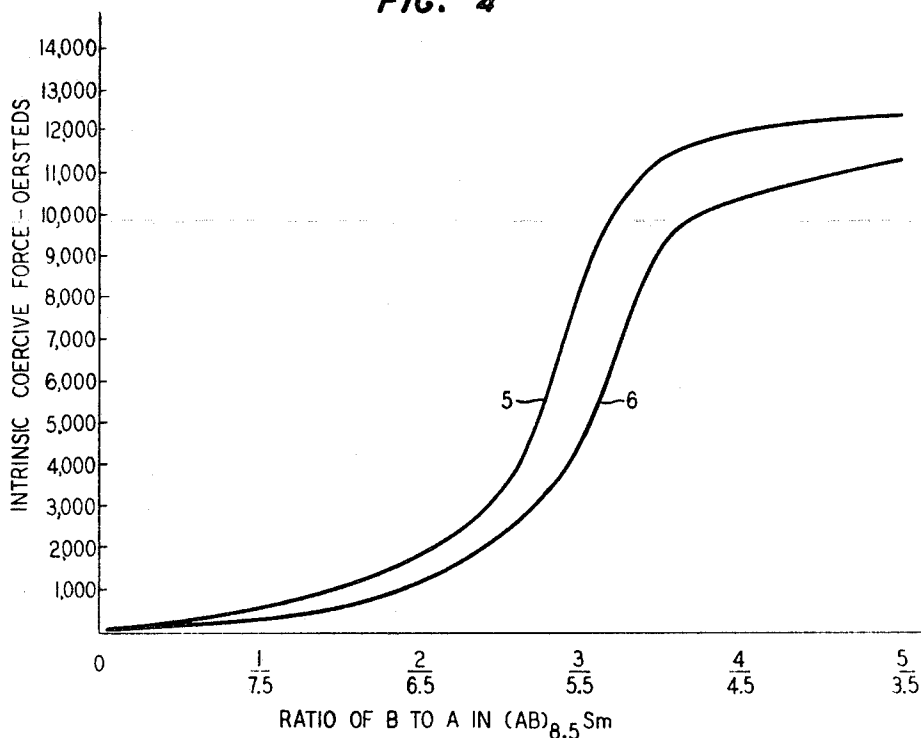
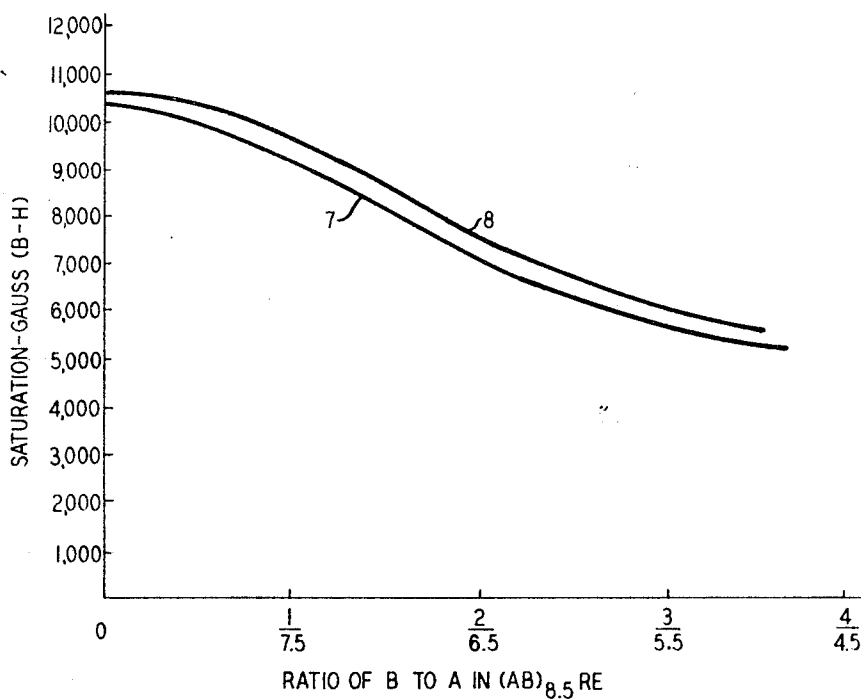


FIG. 5



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**PERMANENT MAGNETIC MATERIALS**

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Filed Apr. 1, 1968, Ser. No. 717,671  
Int. Cl. C22c 19/00, 39/00

U.S. Cl. 75—122

17 Claims

**ABSTRACT OF THE DISCLOSURE**

The specification describes magnetic compositions of the ternary system Co-Cu-Rare earth and related compositions wherein the cobalt may be partially or completely substituted with iron, aluminum or nickel. Certain of the included compositions have coercivities of many thousands of oersteds.

**BACKGROUND OF THE INVENTION**

(1) Field of the invention

The invention is concerned with permanent magnet materials some of which manifest exceedingly high coercivities and to methods for their preparation. Exemplary materials may have large energy products and, in consequence, are useful in applications such as torque drives, loud speakers, motors, and the like in which the magnetic circuit usually includes an air gap.

(2) Description of the prior art

As summarized in 38 #3 Journal of Applied Physics, page 1001 (March 1967), it has been known for some time that certain intermetallic compounds of many of the lanthanide rare earth metal and related elements have permanent magnetic properties in powder form. These materials of composition, such as  $\text{Co}_3\text{Y}$ ,  $\text{Co}_3\text{Ce}$ , etc., have extremely high crystalline anisotropy and high coercivities. In fact, coercivities of 9000 oersteds and higher than been measured on particles sufficiently small to inhibit substantial domain wall motion (particles of the order of 10 microns). While as reported in the cited reference, these materials are considered promising for fine particle permanent magnets, attempts to retain permanent magnet properties in solid bodies have been unavailing.

**SUMMARY OF THE INVENTION**

The invention is in a series of permanent magnet compositions and methods for their preparation. The inventive compositions lie in specific regions of the ternary system represented by  $\text{AB}(\text{RE})$  where A is iron or cobalt or a mixture thereof, B is copper, nickel or aluminum or mixtures of copper with aluminum or nickel, and (RE) is the rare earth samarium or another rare earth such as gadolinium, praseodymium, samarium, cerium, neodymium, holmium or the rare earth-related elements lanthanum and yttrium substituted in their entirety or admixed in lesser amounts. For convenience all of the latter group of elements are referred to as rare earth elements represented by the symbol (RE).

Certain of these compositions, those which fall on the stoichiometric line between the  $\text{A}_5(\text{RE})$  and  $\text{B}_5(\text{RE})$  pseudo-binaries are described and claimed in the application of E. A. Nesbitt and R. H. Willens, Ser. No. 717,672, filed concurrently herewith. In these compounds the stoichiometric relationship of five trivalent cations for each rare earth anion is preserved throughout. However, this stoichiometric relationship does not follow the usual ionic relationship and thus suggests the existence of related compounds which do not possess a total of six ions.

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It has now been found that compositions which deviate from those having  $(\text{AB})_5(\text{RE})$  stoichiometry can be prepared and exhibit magnetic properties comparable to those of the  $(\text{AB})_5(\text{RE})$  compounds. These compositions fall within the region bounded by the  $\text{A}_5(\text{RE})$ - $\text{B}_5(\text{RE})$  and  $\text{A}_{17}(\text{RE})_2$  and  $\text{B}_{17}(\text{RE})$  pseudo-binaries between 20 percent and 100 percent A and 2 percent to 100 percent B. The percents given in this description refer in every case to atomic percents.

In each case it is the A component, cobalt, iron or cobalt-iron mixtures, that provides the magnetic properties. Diluting the A component with element B decreases the saturation magnetization of the overall composition. The non-magnetic component B is responsible for minimizing or eliminating domain wall motion so that increasing amounts result in increasing coercivity. The dramatic improvements in coercivity thus obtained contributes one of the unobvious features of the invention. Useful improvements in this regard obtain from the inclusion of component B in amounts of greater than 1.7 atomic percent and less than 71.5 atomic percent. These values correspond to the molar range of 2 percent to 80 percent of component B calculated as  $\text{B}_x(\text{RE})$  where x again is greater than 5 and less than 8.5.

Although these compositions may be referred to as intermetallic compounds it is perhaps more meaningful to allude to the entire composition as a solid solution. In so doing, it should be understood that the terminology is not intended to indicate complete homogeneity. In fact, based on the reported powder work and on general understanding of other permanent magnetic materials, it is most probable that regions of the  $\text{A}_x(\text{RE})$  compound are somehow separated by regions of the  $\text{B}_x(\text{RE})$  compound so as to reduce domain wall motion.

The essence of the invention is the retention of certain permanent magnet properties in comparatively massive bodies. While as-cast bodies show sufficient magnetic properties for many uses, a preferred aspect of the invention derives from the discovery that a low temperature anneal may further enhance these properties. Under certain circumstances still further improvement may be achieved by preparing powders from the cast materials and by carrying out a further series of operations on these powders. For example, they may be oriented within a magnetic field and finally sintered or otherwise fixed in position so as to produce a new solid body. Since the as-cast body shows the general effects of single domain particles it is not necessary to produce powders of the fine sizes required previously.

**BRIEF DESCRIPTION OF THE DRAWING**

FIG. 1 is a ternary composition diagram for the system Co-Cu-RE, where the rare earth is samarium or cerium, describing the compositions within the scope of the invention;

FIG. 2, on coordinates of coercivity in oersteds and composition terms of the atomic ratio of B to A in the general formula  $(\text{AB})_5\text{Sm}$ , is a graph showing the relationship between these two parameters for as-cast and also for subsequently annealed material for the compositional system along the  $\text{A}_5(\text{RE})$ - $\text{B}_5(\text{RE})$  pseudo-binary;

FIG. 3, on coordinates of saturation magnetization B-H, in gauss, and composition in terms of the atomic ratio of B to A in the formula  $(\text{AB})_5(\text{RE})$ , is a graph showing the relationship between these two parameters for two different rare earth-containing compositions;

FIG. 4, on coordinates of coercivity in oersteds, in gauss, and composition in terms of the atomic ratio of B to A in the formula  $(\text{AB})_{8.5}\text{Sm}$ , is a graph showing the relationship between these two parameters for compositions falling along the  $\text{A}_{8.5}\text{Sm}$ - $\text{B}_{8.5}\text{Sm}$  pseudo-binary; and

FIG. 5, on coordinates of saturation magnetization

B-H, in gauss, and composition in terms of the atomic ratio of B to A in the general formula  $(AB)_{8.5}(RE)$ , is a graph showing the relationship between these two parameters for compositions falling along the  $A_{8.5}(RE)-B_{8.5}(RE)$  pseudo-binary.

#### Detailed description

The operative compositions are best described by reference to the ternary diagram of FIG. 1 wherein the compositions of interest are those falling within the shaded area "Z" and which satisfy the relationship:

$$(AB)_x(RE)$$

where  $x$  is greater than 5 to approximately 8.5. The shaded area "Z" can be defined in terms of composition by describing the boundary lines for the shaded area "Z." These lines join the following compositions designated points a, b, c, d:

(a)

	Percent
Co -----	18
Cu -----	71.5
Rare earth -----	10.5

(b)

	Percent
Co -----	16.7
Cu -----	66.6
Rare earth -----	16.7

(c)

	Percent
Co -----	81.6
Cu -----	1.7
Rare earth -----	16.7

(d)

	Percent
Co -----	87.7
Cu -----	1.8
Rare earth -----	10.5

As stated previously, the A component, which is the magnetic component, is cobalt and/or iron. So far it appears that cobalt is to be preferred, since resulting compounds manifest higher coercivities. While coercivities of iron-containing materials are improved in accordance with the invention they are lower than those containing cobalt. Even should this relationship continue, there may nevertheless be occasions in which partial or total substitution of cobalt by iron would be preferred. This arises from the fact that saturation values are increased. By analogy to other magnetic materials, it has been observed the highest saturation values obtained have equal atom amounts of iron and cobalt. A desired partial range is set at a maximum value of about 60 atom percent iron. A preferred lower limit may be set at 2 atom percent iron. These limits are prescribed on the basis that the partial substitution is made to increase saturation magnetization. Inclusion of exceedingly small amounts of iron increases saturation although appreciable increase is realized only by use of the minimum value set forth. Use of amounts appreciably in excess of the maximum values results in no further increase in saturation and at the same time decreases the coercivity associated with the cobalt containing compound.

The "B" component of the system is Cu, Al, or Ni or mixtures of Cu with Al and Ni. Best results thus far obtained have been on copper containing compositions although a large part of the magnetic improvement is retained by total or partial substitution of copper by aluminum and/or nickel. It has been observed that atom percentages of the elements, copper, nickel, and/or aluminum, may desirably range from 2 atom percent to 80 atom percent based on the total number of atoms of these elements together with cobalt and/or iron.

From the foregoing description, it is clearly desirable to utilize as little as possible of a copper, nickel and/or

aluminum compound since it makes little magnetic contribution to the final composition at usual operating temperatures. It is characteristic that increasing substitution of the cobalt and/or iron-containing compounds may produce first an increasing and finally a decreasing coercivity while at the same time resulting in a constantly decreasing saturation. This behavior is evidenced by the figures. Based on such observations and assuming the desirability of high coercivity together with high energy product, it is possible to define a more preferred compositional range as that in which the ratio of B to A approximates the range of from about 0.2 to about 1.5. Of course, other considerations based on specific device needs may suggest the use of compositions outside this preferred range. Whereas 8.5 formula units for the A and B components has been discussed as a convenient maximum it is evident that these mixtures are not stoichiometric and that this value can be exceeded somewhat while still obtaining the unexpected advantages of this invention.

The final choice of range of non-magnetic compound cation inclusion is dependent, to some extent, on processing conditions. Increasing cooling rate from the reaction temperature results in increasing coercivity so lending further credence to the assumption that there is present, in the final composition, a high temperature phase precipitate at least with respect to one or the other of the two compounds. Also, while the broad limits set forth are desirable in all included systems, certain compositional or processing deviations may give rise to peak values of coercivity in a somewhat altered preferred range.

The inventive concept has been adequately described. It relies on the retention of permanent magnet properties in bodies substantially larger than single domain particles.

This effect may be retained in bodies containing a variety of compositional ingredients. For example, some oriented samples have been prepared by powdering solid specimens (50 microns or larger particles), imbedding them in a matrix such as a wax and orienting them within an applied field. It is clear that relative amounts of matrix material may be exceedingly large. In principle, permanent magnetic effects are retained even in bodies in which particles are separated by dimension orders of magnitude larger than the particles.

While certain additives may be incorporated to modify certain of the magnetic properties, additives of most significance from a coercivity or saturation standpoint have already been set forth. Other ingredients may include elements such as iron to increase permeability and elements such as vanadium to improve mechanical properties such as workability. Unintentional ingredients are not generally significant in amounts ordinarily incorporated in accordance with commercial processing deviations. Such inclusions which may total one or very few weight percent as well as significantly larger inclusions can have little effect on the structure of the compound making the magnetic contribution.

Since, however, high energy product is frequently desirable and since non-magnetic inclusions are likely to dilute this value, a preferred compositional range assumes no more than 10 weight percent of additional ingredients in solution in either or both of the mixed compounds. This preferred limit is not indicated to impose any limitation upon the presence of additional phases such as illustrated by a wax matrix.

Some of the prior work on mixed compounds of the transition metal containing variety have utilized mischmetal in lieu of a pure rare earth. One variety predominating in cerium costs as little as a few dollars per pound as compared with prices at least in order of magnitude higher for single rare earths. This and other types of mischmetal may be used in the preparation of the inventive compositions.

It is known from previous work that the orbital roles of the electrons of the rare earths cerium, samarium,

praseodymium and neodymium make the permanent magnet less anti-ferromagnetic. Since, in general, the invention permits suitably high coercivities for any of the included compositions, the resultant increase in saturation, and consequently, in energy product results in a preference for these four anions.

#### PROCESSING

It is ordinarily desirable to form the solid solution in accordance with a procedure including a rapid cooling step after reaction. It has been observed that coercivity increases as cooling rate increases, at least over the temperature range, down to about 600° C. There is no experimentally determined limit on this relationship. Materials cooled from the melting point of about 1600° C. to 600° C. in 15 minutes have manifested coercivities of 6000 oersteds as contrasted with 13,000 oersteds for the same composition identically processed but with cooling over the same temperature interval taking place over about one millisecond. It is considered desirable to utilize a cooling rate of at least 1000° per minute, and this is considered to be a preferred limit on this processing step.

An obvious metallurgical method useful in the preparation of the inventive materials is arc melting and some of the results reported herein were obtained from samples prepared by this method. Samples have also been prepared by solidification, float zoning and rapid quenching from the liquid state. Other techniques which permit cooling as outlined above are satisfactory. The only additional requirement on processing is that reactive atmospheric ingredients be excluded since, for example, the rare earth metal elements form hydrides, nitrides and oxides, hydrogen, nitrogen and oxygen should be substantially excluded. It has been found convenient to carry out melting in an inert atmosphere such as argon.

The arc melting method is briefly outlined: The desired quantities of elementary materials in accordance with the designated stoichiometry are weighed out and melted. The apparatus used consists of a water cooled copper hearth with a ¾ inch diameter hemispherical cavity. A second nondisposable electrode, also water cooled, made, for example, of tungsten, is spaced from the surface of the reactants by a fraction of an inch. An arc is struck with a high frequency current (250 amperes or greater) and is maintained with a DC potential sufficient to bring about melting. For a 30 gram total charge, a 30 volt potential at a spacing of .50 inch results in a current of about 500 amperes which was sufficient to bring about melting in a period of about 30 seconds. Cooling from the melting temperature from 1600° C. to about 600° C. is accomplished in a period of about 25 seconds by turning off the furnace power.

A low temperature anneal has been found to result in a substantial increase in coercivity. While some improvement in coercivity has resulted by heating to temperatures as low as 300° C. for periods as short as one hour, peak coercivities have in general been obtained only upon exposure at 300° C. for periods of the order of at least 4 hours. Higher temperature annealing accomplishes the same improvement in a shorter period. Annealing may be carried out at temperatures up to about 700° C. Time required for such elevated temperature to realize measurable improvement in coercivity is of the order of 30 seconds. Peak coercivity is reached in about 30 minutes. Corresponding optimum times at 400° C. and 500° C. are about 4 hours and one hour respectively.

The mechanism to which annealing is due is not completely understood. It seems consistent with experimental observation to postulate some degree of phase participation or crystallographic ordering.

While the invention depends on the retention to permanent magnetic properties in solid bodies of material and so avoids the need for powdering to single domain particle size, it may nevertheless be desirable to powder the as-cast or annealed specimen. One reason for powdering is to

permit orientation which may be carried out at temperatures approaching the Curie temperatures (generally of the order of a few hundred degrees centigrade). In contrast with the prior art single compound material, particles so oriented may subsequently be sintered so as to again produce a solid body. Since the magnetic compound is inherently anisotropic, this additional processing step may result in a significant increase in coercivity. The degree of orientation, of course, depends upon the extent to which single domain particle sizes are approached. While it is not ordinarily expedient to produce powders as fine as the 10 micron particles previously required, it may be desirable to pulverize as small as about 50 microns. Such pulverized samples represent an advance over prior art single compound samples in that they may be sintered without losing permanent magnet properties.

#### PROPERTIES

The coercivity and saturation magnetization, B-H, for compounds of the general formula (AB)<sub>5</sub>(RE) (where the ratio of B to A varies from zero to four) are shown in FIGS. 2 and 3 respectively. The coercivity and saturation magnetization, B-H, for compounds of the general formula (AB)<sub>8.5</sub>(RE) (where the ratio of B to A varies from zero to above 5/3.5) are shown in FIGS. 4 and 5 respectively. In each case two curves are shown. In FIGS. 2 and 4 the curves 2 and 6 describe the coercivity for the compositions as cast whereas curves 1 and 5 indicate the results of the anneal or aging treatment described above. The improvement obtained as a result of the anneal treatment is evident.

FIGS. 3 and 5 also show two curves. Curves 3 and 7 give the properties of compounds containing samarium as the rare earth and curves 4 and 8 give the properties of compounds containing cerium as the rare earth.

The data gives the properties for the boundary compositions in the shaded area "Z" of FIG. 1 and provides a firm basis for predicting the properties of the included compositions. The coercivity values of other exemplary included compositions are given in the following table.

TABLE I

Material:	H <sub>c</sub> oersteds (as-cast)
Co <sub>4</sub> Cu <sub>1.5</sub> Ce	7500
Co <sub>4</sub> Cu <sub>1.5</sub> Sm	4500
Co <sub>5.07</sub> Cu <sub>1.17</sub> Sm	12300
Co <sub>5.25</sub> Cu <sub>1.5</sub> Ce	21400

<sup>1</sup> 3500 after aging.  
<sup>2</sup> 4800 after aging.

For many purposes, the value of a permanent magnetic material is measured in terms of its energy product. This value which, in a sense, is a measure of the amount of energy which can be put into an air gap is conventionally taken of the product of the magnetization B and the coercivity H at the knee of the hysteresis curve in the second quadrant. For the materials of this invention in which the coercivity is typically much larger than the magnetization, the energy product may be taken as B<sub>sat</sub><sup>2</sup>/4 where B<sub>sat</sub> is the saturation magnetization. Typical values for preferred compositions within the inventive scope are in excess of a million oersted-gauss. Certain of the materials have had measured products of 9 million.

#### USES

The inventive material are distinguished primarily by their large coercivity values. These, of course, suggest use in magnetic circuitry including an air gap. Applications include magnetic bearings, DC motors, and torque drives. As contrasted with the competitive, commercially available, Alnico materials, the inventive compositions may take the form of bodies having relatively short dimensions in their magnetization direction. To compensate for the sometimes larger saturation values available in other materials, magnetic elements may have larger cross sectional areas normal to the magnetic direction. In con-

trast, the best of the prior art commercial materials, while they may take the form of smaller cross-sectional elements, generally must be a greater length so as to increase the anisotropy through shape effect.

The invention has been derived in terms of a number of exemplary embodiments. Certain compositional and processing variations have been noted, others are apparent. The invention is premised on the retention of single domain particle properties in massive bodies of the compositions noted. The retention is attributed to the inclusion of copper, nickel and/or aluminum in any of the listed cobalt and/or iron-containing compounds. The following claims are to be so construed.

As a further example, since the main magnetic contribution is made by the cobalt and/or iron cation with the rare earth contribution being largely anti-ferromagnetic, it may be desirable to replace the rare earth at least in part by a different anion known to yield an isostructural compound. Much of the prior art work has been based on the structure of  $\text{Cu}_5\text{Ca}$ , and calcium is accordingly a prime candidate. Other elements which may be used include strontium and barium.

Various additional modifications and extensions of this invention will become apparent to those skilled in the art. All such variations and deviations which basically rely on the teachings through which this invention has advanced the art are properly considered within the spirit and scope of this invention.

What is claimed is:

1. A magnetic composition consisting essentially of a solid solution falling within the shaded area "Z" of FIG. 1, and wherein the ternary component (RE) is at least one element selected from the group consisting of samarium, cerium, gadolinium, praseodymium, lanthanum, yttrium, neodymium, and holmium, A is at least one element selected from the group consisting of cobalt and iron, B contains copper, and the amount of (RE) is less than  $\frac{1}{2}$  of the formula units of the composition.

2. A magnetic composition consisting essentially of a solid solution having the general formula  $(\text{AB})_x(\text{RE})$  in which A is at least one element selected from the group consisting of cobalt and iron, B contains copper, (RE) is at least one element selected from the group consisting of samarium, cerium, gadolinium, praseodymium, lanthanum, yttrium, neodymium, and holmium, and  $x$  has a value greater than 5 and up to approximately 8.5.

3. The composition of claim 2 wherein the atomic ratio of B to A lies in the range of 0.2 to 1.5.

4. Composition of claim 2 in which A is cobalt containing up to 60 atom percent iron.

5. Composition of claim 2 in which (RE) is at least 50 atom percent cerium.

6. Composition of claim 2 in which (RE) is at least 50 atom percent samarium.

7. Process for forming a permanent magnet material comprising admixing reactants which will yield a composition, containing at least one element selected from

a group consisting of cobalt and iron together with at least one element selected from the group consisting of samarium, cerium, gadolinium, praseodymium, lanthanum, yttrium, neodymium and holmium, heating to the melting point, and cooling to form a compound of the stoichiometry  $M_5(\text{RE})$ , characterized in that there is additionally admixed with said reactants material which will yield copper, and in that the composition of the said reactants is such that the final composition may be represented by the approximate formula  $(\text{AB})_x(\text{RE})$  as defined in claim 2.

8. Process of claim 7 in which cooling over the temperature range of from about 1600° C. to about 600° C. is carried out of a maximum time interval of 15 minutes.

9. Process of claim 8 in which the said time interval is a maximum of about one minute.

10. Process of claim 7 in which the said composition is maintained at a temperature of from 300° C. to 700° C. for a period of from four hours to 30 seconds, the longer times corresponding with the lower temperatures.

11. Process of claim 10 in which the said composition is maintained within the said temperature range for a period of from about 10 minutes to about 30 seconds.

12. Process of claim 7 in which the resultant composition is pulverized and in which the resultant powder is magnetically oriented.

13. Process of claim 12 in which the oriented powder particles are fixed in a relative position.

14. Process of claim 13 in which the said relative positions are fixed by sintering.

15. Process of claim 13 in which the oriented particles are frozen in a matrix.

16. Product produced in accordance with the process of claim 10.

17. Product produced in accordance with the process of claim 13.

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L. DEWAYNE RUTLEDGE, Primary Examiner

J. E. LEGRU, Assistant Examiner

U.S. Cl. X.R.

75—0.5, 123, 129, 170; 148—31.57, 101, 102, 103

**Notice of Adverse Decisions in Interferences**

In Interference No. 97,836 involving Patent No. 3,560,200, E. A. Nesbitt, J. H. Wernick, and R. H. Willens, PERMANENT MAGNETIC MATERIALS, final judgment adverse to the patentees was rendered Feb. 8, 1973, as to claim 2.

*[Official Gazette March 27, 1973.]*