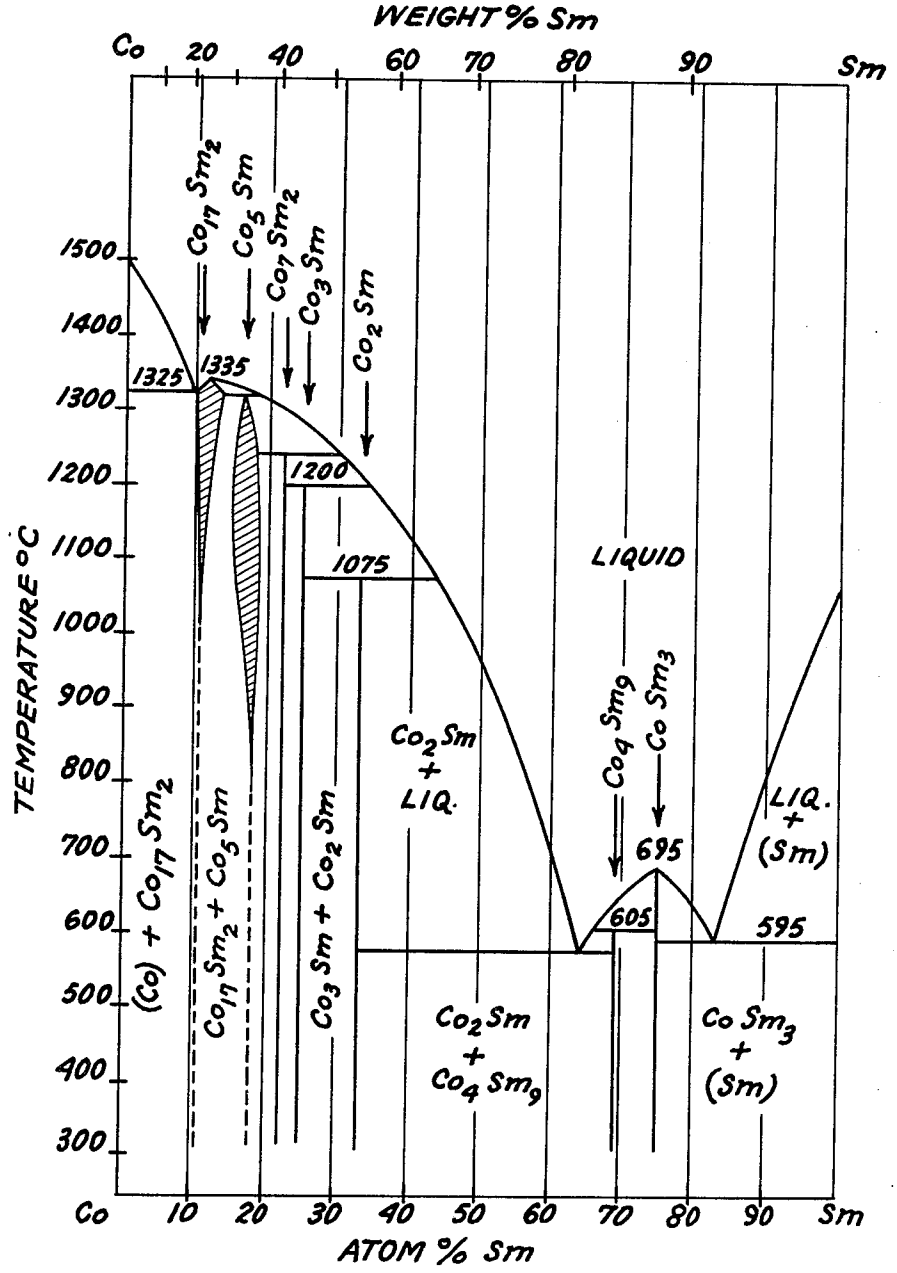
Oct. 3, 1972 M. G. BENZ 3,695,945

METHOD OF PRODUCING A SINTERED COBALT-RARE EARTH INTERMETALLIC PRODUCT

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Fig. 1.



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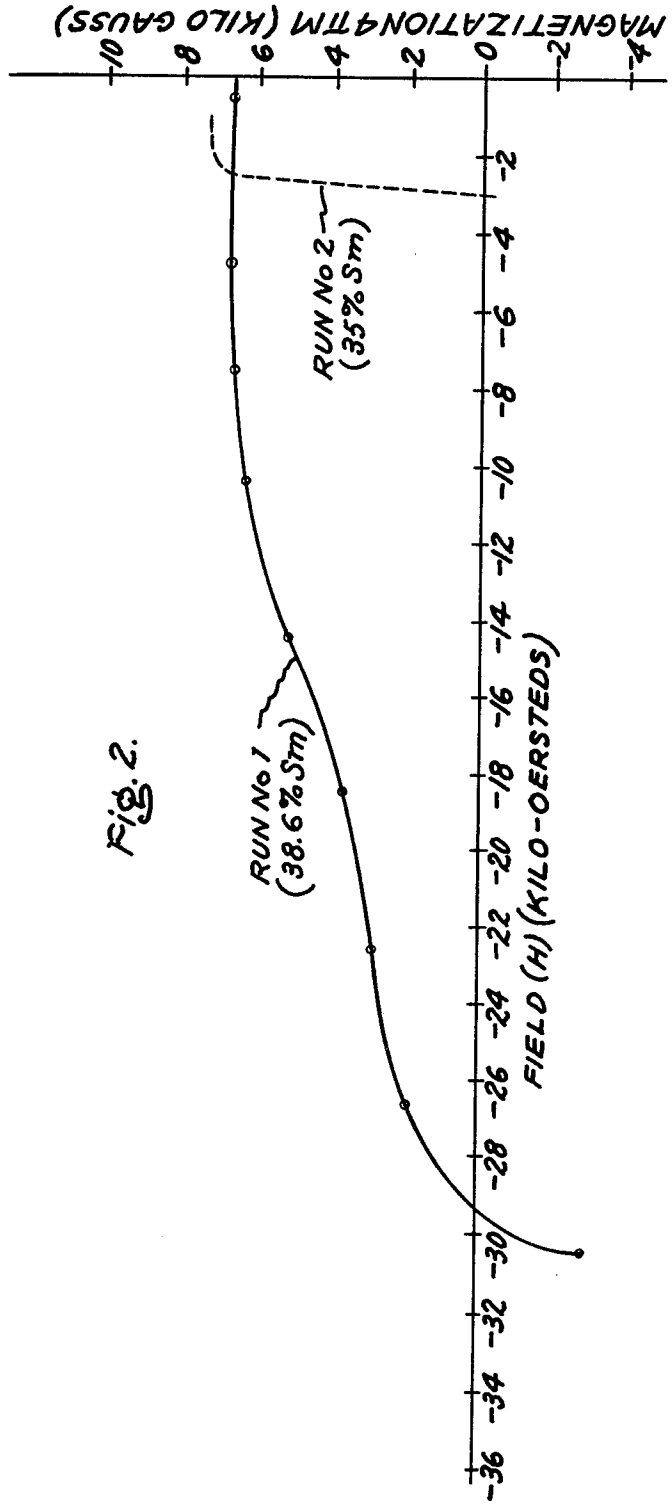


Fig. 2.

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3,695,945

METHOD OF PRODUCING A SINTERED COBALT-RARE EARTH INTERMETALLIC PRODUCT

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U.S. Cl. 148—103 12 Claims

ABSTRACT OF THE DISCLOSURE

A process for preparing novel sintered cobalt-rare earth intermetallic products which can be magnetized to form permanent magnets having stable improved magnetic properties. A cobalt-rare earth metal alloy is formed having a composition which at sintering temperature falls outside the composition covered by the single Co_5R intermetallic phase on the rare earth richer side. The alloy contains a major amount of the Co_5R intermetallic phase and a second solid CoR phase which is richer in rare earth metal content than the Co_5R phase. The specific cobalt and rare earth metal content of the alloy is substantially the same as that desired in the sintered product. The alloy, in particulate form, is pressed into compacts and sintered to the desired density. The sintered product is comprised of a major amount of the Co_5R solid intermetallic phase and up to about 35 percent by weight of the product of the second solid CoR intermetallic phase which is richer in rare earth metal content than the Co_5R phase.

SINTERED COBALT-RARE EARTH INTERMETALLIC PRODUCT

The present invention relates generally to the art of permanent magnets and is more particularly concerned with novel sintered cobalt-rare earth intermetallic products having unique characteristics and with a sintering method for producing such products.

Permanent magnets, i.e. "hard" magnetic materials such as the cobalt-rare earth intermetallic compounds, are of technological importance because they can maintain a high, constant magnetic flux in the absence of an exciting magnetic field or electrical current to bring about such a field.

Cobalt-rare earth intermetallic compounds exist in a variety of phases, but the Co_5R intermetallic single phase compounds (in each occurrence R designates a rare earth metal) have exhibited the best magnetic properties. The permanent magnet properties of bulk Co_5R, as well as cobalt-rare earth intermetallic magnetic materials generally, can be enhanced by reducing the bulk bodies to powders, but in such finely-divided form these materials are unstable in air and their magnetic properties deteriorate after a short period of time.

It is an object of the present invention to provide cobalt-rare earth intermetallic magnets which have superior magnetic properties and are stable in air.

Those skilled in the art will gain a further and better understanding of the present invention from the detailed description set forth below, considered in conjunction with the figures accompanying and forming a part of the specification, in which:

FIG. 1 is the cobalt-samarium phase diagram. It is assumed herein, that the phase diagram at 300° C., which

is the lowest temperature shown in the figure, is substantially the same at room temperatures.

FIG. 2 is a chart bearing curves which illustrate the effect of samarium content on the magnetic properties of permanent magnets including one produced in accordance with the present invention.

Briefly stated, the process of the present invention comprises the steps of forming a particulate cobalt-rare earth metal alloy, compacting the alloy particles to produce a green body, and sintering the green body to produce an ultimate sintered body containing a major amount of Co_5R phase and up to 35 percent of other cobalt-rare earth phases richer in rare earth metal content than Co_5R.

The composition of the cobalt-rare earth metal alloy of the present invention falls outside the composition covered by the single Co_5R intermetallic phase composition on the rare earth richer side at sintering temperature. Since sintering does not affect the cobalt and rare earth metal content of the alloy, or does not affect it to any significant extent, the amount of cobalt and rare earth metal used in forming the alloy are substantially the same as those desired in the sintered product. The present sintered product contains a major amount of the Co_5R phase and up to 35 percent of a CoR phase which is richer in rare earth metal content than the Co_5R phase. The specific alloy composition can be determined from the phase diagram for the particular cobalt-rare earth metal system or empirically. For example, FIG. 1 shows that for the cobalt-samarium system, the alloy composition useful in forming the particular sintered product of the present invention has a samarium content ranging from about 36 to about 39 percent by weight.

The rare earth metals useful in forming the present cobalt-rare earth metal alloys and intermetallic compounds are the 15 elements of the lanthanide series having atomic numbers 57 to 71 inclusive. The element yttrium (atomic number 39) is commonly included in this group of metals and, in this specification, is considered a rare earth metal. A plurality of rare earth metals can also be used to form the present desired cobalt-rare earth alloys or intermetallic compounds which, for example may be ternary, quaternary or which may contain an even greater number of rare earth metals as desired.

Representative of the cobalt-rare earth metal alloys useful as base and additive alloys in the present invention are cobalt-cerium, cobalt-praseodymium, cobalt-neodymium, cobalt-promethium, cobalt-samarium, cobalt-europium, cobalt-gadolinium, cobalt terbium, cobalt-dysprosium, cobalt-holmium, cobalt-erbium, cobalt-thulium, cobalt-ytterbium, cobalt-lutecium, cobalt-yttrium, cobalt-lanthanum and cobalt-misch metal. Cerium misch metal is the most common alloy of the rare earth metals which contains the metals in the approximate ratio in which they occur in their most common naturally occurring ores. Examples of specific ternary alloys include cobalt-samarium-cerium misch metal, cobalt-cerium-praseodymium, cobalt-yttrium-praseodymium, and cobalt - praseodymium-misch metal.

In forming the alloy in the present process, the cobalt and rare earth metal are each used in amounts substantially corresponding to those desired in the final sintered product. The alloy can be formed by a number of methods. For example, it can be prepared by arc-melting the cobalt and rare earth metal together in the proper amounts under a substantially inert atmosphere such as

argon and allowing the melt to solidify. Preferably, the melt is cast into an ingot.

The alloy can be converted to particulate form in a conventional manner. Such conversion can be carried out in air at room temperature since the alloy is substantially non-reactive. For example, the alloy can be crushed by mortar and pestle and then pulverized to a finer form by jet milling.

The particle size of the cobalt-rare earth alloy of the present process may vary. It can be in as finely divided a form as desired. For most applications, average particle size will range from about 1 micron or less to about 10 microns. Larger sized particles can be used, but as the particle size is increased, the maximum coercive force obtainable is lower because the coercive force generally varies inversely with particle size. In addition, the smaller the particle size, the lower is the sintering temperature which may be used.

The particulate alloy can be compressed into a green body of the desired size and density by any of a number of techniques such as hydrostatic pressing or methods employing steel dies. Preferably, the particulate alloy is compressed in the presence of an aligning magnetizing field to magnetically align the particles along their easy axis, or if desired, the particulate alloy can be compressed after magnetically aligning the particles. The greater the magnetic alignment of the particles, the better are the resulting magnetic properties. Preferably also, compression is carried out to produce a green body with as high a density as possible, since the higher its density, the greater the sintering rate. Green bodies having a density of about forty percent or higher of theoretical are preferred.

The green body is sintered to produce a sintered body of desired density. Preferably, the green body is sintered to product a sintered body wherein the pores are substantially non-interconnecting. Such non-interconnectivity stabilizes the permanent magnet properties of the product because the interior of the sintered product or magnet is protected against exposure to the ambient atmosphere.

The sintering temperature used in the present process depends largely on the particular cobalt-rare earth alloy to be sintered, and to a lesser degree, on particle size. The minimum sintering temperature must be sufficiently high for sintering to occur in a particular cobalt-rare earth system, i.e. it must be high enough to coalesce the particles. Preferably, sintering is carried out so that the pores in the sintered product are substantially non-interconnecting. A sintered body having a density of at least about 87 percent of theoretical is generally one wherein the pores are substantially non-interconnecting. Such non-interconnectivity is determined by standard metallographic techniques, as for example, by means of transmission electron micrographs of a cross-section of the sintered product. The maximum sintering temperature is preferably one at which significant growth of the component particles or grains does not occur, since too large an increase in grain size deteriorates magnetic properties such as coercive force. The green body is sintered in a substantially inert atmosphere such as argon, and upon completion of the sintering, it is preferably cooled to room temperatures in a substantially inert atmosphere.

The particular sintering temperature range can be determined empirically, as for example, carrying out a series of runs at successively higher sintering temperatures and then determining the magnetic properties of the sintered products. For cobalt-samarium alloys of the present invention, a sintering temperature ranging from about 950° C. up to about 1200° C. is suitable with a sintering temperature of 1100° C. being particularly satisfactory.

The density of the sintered product may vary. The particular density depends largely on the particular permanent magnet properties desired. Preferably, to obtain a product with substantially stable permanent magnet properties, the density of the sintered product should be one wherein the pores are substantially non-interconnecting and this occurs usually at a density or packing of about 87 percent. Generally, for a number of applications, the density may range from about 80 percent to 100 percent. For example, for low temperature applications, a sintered body having a density ranging down to about 80 percent may be satisfactory. The preferred density of the sintered product is one which is the highest obtainable without producing a growth in grain size which would deteriorate magnetic properties significantly, since the higher the density the better are the magnetic properties. For cobalt-samarium sintered products of the present invention, a density of at least about 87 percent of theoretical, i.e. of full density, and as high as about 96 percent of theoretical is preferred to produce permanent magnets with suitable magnetic properties which are substantially stable.

In the present invention, at sintering temperature as well as at room temperatures, the final sintered product contains a major amount of the Co_5R solid intermetallic phase, generally at least about 65 percent by weight of the product, and up to about 35 percent by weight of the product of a second solid CoR intermetallic phase which is richer in rare earth metal content than the Co_5R phase. Traces of other cobalt-rare earth intermetallic phases, in most instances less than one percent by weight of the product, may also be present. Sintered products having the highest energy products are those having the smallest content of the second CoR phase. The preferred final sintered product, therefore, is comprised predominantly of the Co_5R intermetallic phase, i.e. about 95 percent by weight or higher but less than 100 percent, with only a detectable content of the second CoR phase, i.e. 5 percent or lower by weight of the product. If desired, for a particular cobalt-rare earth metal system of the present invention, a composition scan, i.e. a series of runs at the same sintering temperature with alloys of proportionately varying composition, may be made to determine the specific sintered product composition which produces the best magnetic properties. Determination of the second CoR phase can be made by a number of techniques, such as for example, X-ray diffraction, electron microscope as well as standard metallographic analysis. As the content of the Co_5R intermetallic single phase is decreased in the present sintered product, the magnetic properties obtainable decrease correspondingly. Furthermore, when the content of the Co_5R intermetallic phase is below about 65 percent by weight of the present sintered product, its permanent magnet properties are sharply reduced.

Magnetization of the sintered product of the present invention results in a permanent magnet with superior magnetic properties. On the other hand, if a final sintered product at sintering or room temperatures consists only of a single Co_5R intermetallic phase, or if it contains a second cobalt-rare earth intermetallic phase of lesser rare earth metal content than that of the Co_5R phase, a permanent magnet of only inferior magnetic properties can be produced no matter how the magnetization step is carried out.

Standard metallographic examination, of a polished cross-section of the present sintered product, as for example, under a light microscope or an X-ray microprobe, shows that its grains differ in appearance from the original particles used in forming the green body. Specifically, the original particles have an angular rough surface structure. In contrast, substantially all of the grains of the present sintered product are rounded and have a smooth surface. The pores of the sintered product are preferably substantially non-interconnecting. Generally, for the sintered product to have good magnetic properties, the component grains of the bulk product should preferably not have an average size larger than about 30 microns.

The sintered product of the present invention is useful as a permanent magnet. Its permanent magnet properties can be significantly enhanced, however, by sintering it

to a magnetizing field. The resulting permanent magnet is substantially stable in air and has a wide variety of uses. For example, the permanent magnets of the present invention are useful in telephones, electric clocks, radios, television, and phonographs. They are also useful in portable appliances, such as electric toothbrushes and electric knives, and to operate automobile accessories. In industrial equipment, the present permanent magnets can be used in such diverse applications as meters and instruments, magnetic separators, computers and microwave devices.

If desired, the sintered bulk product of the present invention can be crushed to a desired particle size preferably a powder, which is particularly suitable for alignment and matrix bonding to give a stable permanent magnet. The matrix material may vary widely and may be plastic, rubber or metal such as, for example, lead, tin, zinc, copper or aluminum. The powder-containing matrix can be cast, pressed or extruded to form the desired permanent magnet.

All parts and percentages used herein are by weight unless otherwise noted.

The invention is further illustrated by the following examples in which, unless otherwise noted, the conditions and procedure were as follows:

The aligning magnetizing field was used to magnetically align along the easy axis.

The sintering furnace was a ceramic tube.

All sintering was carried out in an inert atmosphere of purified argon and upon completion of the sintering, the sintered product was cooled in the same purified argon atmosphere.

Particle size was determined by a standard metallographic method.

The density of the green body as well as the sintered product is given as packing. Packing is the relative density of the material, i.e. it is a percent of theoretical. Packing was determined by a standard method using the following equation:

$$\frac{\frac{\text{weight}}{\text{volume}}}{8.5\ \text{g./cc.}} \times 100 = \text{Percent packing}$$

where 8.5 g./cc. is the density of Co_5Sm.

The intrinsic coercive force H_{ci} or $_mH_c$ is the field strength at which the magnetization (B–H) or $4\pi M$ is zero.

Normal coercive force H_c is the field strength at which the induction B becomes zero.

The maximum energy product $(BH)_{max}$ represents the maximum product of the magnetic field H and the induction B determined on the demagnetization curve.

EXAMPLE 1

In this example, the magnetic properties of a sintered product of the present invention were determined and compared to those of a control sintered product consisting of a single Co_5Sm phase.

For Run No. 1 of Table I, which illustrates the present invention, a cobalt-samarium alloy melt was made under purified argon by arc-melting and then cast into an ingot. The melt was formed from 61.4% by weight cobalt and 38.6% by weight samarium. The ingot was initially crushed by means of mortar and pestle and then reduced by fluid energy "jet" milling to a powder ranging in size from approximately 1 to 10 microns in diameter and having an average particle size of about 6 microns. Standard wet chemical analysis of the powder showed a content of 38.6% samarium. A bar was formed from a portion of this alloy powder. Specifically, the powder sample was weighed, placed in a rubber tube and magnetically aligned therein by means of an aligning magnetizing field of 60 kilo-oersteds provided by a superconducting coil. After magnetic alignment, the tube was evacuated to freeze the alignment and then it was pressed hydrostatically under a pressure of 200K p.s.i. to form a green body in the shape of a bar.

The green body was then sintered and its properties determined after sintering. After magnetization at room temperatures in a field of 100 kilo-oersteds, the magnetic properties of the sintered product were determined.

The procedure used in Run No. 2 of Table I, which is the control, was the same as that used in Run No. 1 except that the alloy powder was formed by admixing 9.51 grams of a 33.3% by weight samarium—66.7% by weight cobalt alloy powder with 4.49 grams of a 38.6% by weight samarium—61.4% by weight cobalt alloy powder to form a mixture composed of 65% by weight cobalt and 35% by weight samarium. Standard wet chemical analysis of the control powder showed a content of 35±0.3% samarium.

Table I illustrates the specific procedure used for each run.

TABLE I

Run No.	Composition, weight percent Co	Sm	Compaction pressures (K p.s.i.)	Green body: Weight (grams)	Size (inches): Diameter	Length	Packing (percent)	Sintering method: Time, hours	Temperature, (° C.)	Sintered product: Weight (grams)	Size (inches): Diameter	Length	Packing (percent)	Magnetic properties of sintered product after magnetization: Maximum energy [1]	Intrinsic coercive force $_mH_c$ (K oersteds)
1	61.4	38.6	200	11.70	.325	1.267	79	20	1,100	11.71	.315	1.205	88.5	13.2	−25.0
2 (Control)	65	35	200	10.17	.300	1.275	80	½	1,100	10.16	.296	1.256	83.4	11	−2.8

[1] Produced $(BH)_{max}$. (10^6 gauss×oersteds).

Run No. 1 of Table I illustrates the present invention and shows the significantly better magnetic properties produced by the present process. Specifically, Runs Nos. 1 and 2 of Table I show that sintering of the green body produces a sintered product which weighs the same as the green body indicating no loss in the cobalt and samarium components. A comparison of the composition of Run No. 1 with that of Run No. 2 shows the criticality of sintering a cobalt-samarium alloy having a composition falling outside that covered by the single Co_5Sm intermetallic phase on the rare earth richer side.

The sintered bars of Run Nos. 1 and 2 were demagnetized using the specific magnetizing fields shown in FIG. 2 and their magnetization $4\pi M$ in such fiield as determined.

In FIG. 2, the abscissa of the graph is the magnetic field (H) in kilo-oersteds and the ordinate is magnetization $4\pi M$ in kilo-gauss. From the demagnetization curves of FIG. 2, it can be seen that the product of Run No. 1 containing 38.6% by weight samarium has the best magnetic properties. This is particularly illustrated by its high intrinsic coercive force. As can be seen from the phase diagram of FIG. 1, this product at the sintering temperature of 1100° C. as well as at room temperature is comprised of a major amount of the Co_5Sm single intermetallic phase, i.e. about 67% by weight of the product, and the Co_7Sm_2 phase in an amount of about 33% by weight of the product.

FIG. 2 shows poor magnetic properties for the sintered product of Run No. 2 composed of 65% cobalt and 35% by weight samarium which according to FIG. 1 is the composition for a single Co_5Sm intermetallic phase.

The sintered product of each run of Table I was examined by standard metallographic analysis. Examina-

tion of a polished cross-section of each product was made under an X-ray microprobe and a light microscope and micrographs were made. In Run No. 1, the pores of the sintered product were substantially non-interconnecting which is the characteristic that maintains its permanent magnet properties stable. The Run No. 1 sintered product was composed of two phases, a major amount of one phase and a minor amount of a second phase with traces of a few other phases. Substantially all of the grains of this sintered product were rounded and had a smooth surface with the average grain size being about 7 microns. In Run No. 2 the sintered product was composed of only a single intermetallic phase and had some interconnection of pores.

EXAMPLE 2

After five months in air at room temperature the intrinsic coercive force of the sintered product of Run No. 1 of Example 1 was determined and found to be unchanged. This illustrates the highly stable properties of the permanent magnets of the present invention.

EXAMPLE 3

In this example, the properties of a sintered product consisting of a single Co_5Sm phase were determined.

The procedure used in this example was the same as that used in Run No. 2 of Example 1 except that the alloy powder was formed by admixing 13.95 grams of 33.3% by weight samarium—66.7% by weight cobalt alloy powder with 0.41 gram of a 77% by weight cobalt—23% by weight samarium powder to form a mixture composed of 67% by weight cobalt and 33% by weight samarium. A portion of this mixture was formed into a green body in the same manner as in Run No. 2 of Example 1 except that an aligning magnetizing field of 100 kilo-oersteds was used. It had an estimated packing of 81% based on those measured for similar samples.

The green body was sintered at a temperature of 1100° C. for ½ hour. The sintered body weighed 6.73 grams and was 0.265 inch in diameter and 1.055 inches in length and had a packing of 83%. After magnetization in a field of 100 kilo-oersteds, its intrinsic coercive force was determined to be −1.7 kilo-oersteds and it had a maximum energy product $(BH)_{max.}$ of 6×10^6 gauss×oersteds.

Standard metallographic analysis of this product showed it to consist of a single intermetallic phase with some interconnection of the pores.

Standard wet chemical analysis of this sintered product showed it to contain 33% by weight samarium. Sintering, therefore, does not affect the cobalt or samarium content of the composition.

All of the following cited copending patent applications are, by reference, made part of the disclosure of the present application.

In copending U.S. patent application Ser. No. 33,348 entitled "Sintered Cobalt-Rare Earth Intermetallic Product and Process Using Solid Sintering Additive," filed of even date herewith in the name of Mark G. Benz and assigned to the assignee hereof there is disclosed a process for preparing novel sintered cobalt-rare earth intermetallic products by forming a particulate mixture of a base cobalt-rare earth alloy, which at sintering temperature exists as a solid Co_5R intermetallic phase, and an additive cobalt-rare earth alloy, which at sintering temperature is a solid, compacting the mixture to produce a green body and sintering the green body to produce a sintered product containing a major amount of Co_5R and up to about 35% by weight of the product of a second solid CoR intermetallic phase which is richer in rare earth metal content than the Co_5R phase.

In copending U.S. patent application Ser. No. 33,315 entitled "Heat-Aged Sintered Cobalt-Rare Earth Intermetallic Product and Process," filed of even date herewith in the names of Mark G. Benz and Donald L. Martin and assigned to the assignee hereof and now abandoned, there is disclosed a process for preparing heat-aged novel sintered cobalt-rare earth intermetallic products by providing a sintered cobalt-rare earth intermetallic product composed of Co_5R intermetallic phase or a major amount of Co_5R intermetallic phase, and heat-aging said product to precipitate out of the Co_5R phase a CoR phase richer in rare earth metal content than the Co_5R phase in an amount sufficient to increase either its intrinsic coercive force H_{ci} and/or normal coercive force H_c by at least 10 percent.

In copending U.S. patent application Ser. No. 33,347 entitled "Liquid Sintered Cobalt-Rare Earth Intermetallic Product" filed of even date herewith in the name of Mark G. Benz and assigned to the assignee hereof, there is disclosed a process for preparing novel sintered cobalt-rare earth intermetallic products by forming a particulate mixture of a base cobalt-rare earth alloy, which at sintering temperature exists as a solid Co_5R intermetallic single phase, and an additive cobalt-rare earth alloy, which at sintering temperature is at least partly liquid, compacting the mixture to produce a green body and sintering the green body to produce a sintered product containing a major amount of Co_5R phase and up to about 35% by weight of the product of a second solid CoR intermetallic phase which is richer in rare earth metal content than the Co_5R phase.

What is claimed is:

1. A process for producing a sintered cobalt-rare earth intermetallic product having substantially stable permanent magnet properties which comprises providing an alloy of cobalt and rare earth metal in particulate form, said cobalt and rare earth metal being used in amounts substantially corresponding to that desired in the sintered product and being comprised of a major amount of Co_5R intermetallic phase and a second phase of CoR which is richer in rare earth metal content than said Co_5R phase, pressing said particulate alloy into a green body and sintering said green body in a substantially inert atmosphere to produce a sintered product having a density of at least about 87 percent of theoretical and consisting essentially of the Co_5R intermetallic phase in an amount of at least about 65 percent by weight of the product and the second CoR intermetallic phase which is richer in rare earth metal content than said Co_5R phase in an amount having a value ranging up to about 35 percent by weight of the product, where R is a rare earth metal or metals.

2. A process for producing a sintered cobalt-rare earth intermetallic product according to claim **1** wherein said rare earth metal is samarium.

3. A process according to claim **2** wherein said samarium ranges from about 36 to about 39% by weight of said alloy.

4. A process according to claim **2** wherein said alloy is composed of about 62% by weight cobalt and 38% by weight samarium.

5. A process according to claim **2** wherein said sintering temperature ranges from about 950 to about 1200° C.

6. A process according to claim **1** wherein said pressing of said particulate alloy into a green body is carried out in an aligning magnetizing field.

7. A process according to claim **1** wherein the particle size of said alloy ranges from about 1 to 10 microns.

8. A process according to claim **1** wherein said sintered product contains said Co_5R intermetallic phase in an amount of about 95 percent by weight of said sintered product.

9. A process according to claim **8** wherein R is samarium.

10. A process according to claim **1** which includes the steps of crushing said sintered product into particles, and bonding the resulting particles of sintered product to a matrix material.

11. A process according to claim **1** which includes the step of subjecting said sintered product to a magnetizing field to produce a magnetized sintered product.

12. A process according to claim 10 which includes the step of subjecting said bonded particles in said matrix material to a magnetizing field to magnetize said particles.

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