United States Patent

Benz

[15] **3,655,464**

[45] **Apr. 11, 1972**

[54] **PROCESS OF PREPARING A LIQUID SINTERED COBALT-RARE EARTH INTERMETALLIC PRODUCT**

[72] Inventor: **Mark G. Benz**, Burnt Hills, N.Y.

[73] Assignee: **General Electric Company**

[22] Filed: **Apr. 30, 1970**

[21] Appl. No.: **33,347**

[52] **U.S. Cl.**...................................**148/101**, 75/200, 75/208, 75/214, 148/31.57, 148/103

[51] **Int. Cl.**..**B22f 3/00, H01f 1/08**

[58] **Field of Search** 75/200, 208, 213, 214; 148/100, 101, 102, 103, 31.57; 29/182

[56] **References Cited**

UNITED STATES PATENTS

3,424,578 1/1969 Strnat et al. 75/213
3,425,828 2/1969 Cape......................................75/200
3,546,030 12/1970 Buschow et al....................148/103 X

OTHER PUBLICATIONS

Westendorp, F. F. et al., Permanent Magnets with Energy Products of 20 Million Gauss Oersteds, Solid State Communications, 1969, pages 639– 640.

Buschow, K. H. J. et al., Intermetallic Compounds in the System Samarium–Cobalt, Journal of the Less Common Metals, Vol. 14, No. 3, March 1968, pages 323– 328.

[57] **ABSTRACT**

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 particulate mixture is formed of a base CoR alloy and an additive CoR alloy, where R is a rare earth metal. The base CoR alloy is one which, at sintering temperature, exists as a solid Co_5R intermetallic single phase. The additive CoR alloy is richer in rare earth metal than the base CoR alloy, and at sintering temperature is at least partly liquid. The base and additive alloys, in particulate form, are each used in an amount to form a mixture which has a cobalt and rare earth metal content substantially corresponding to that of the final desired sintered product. The mixture is pressed into compacts and sintered to the desired sintered product phase composition and density. At sintering temperature, the final sintered product has a phase composition lying outside the Co_5R single phase on the rare earth richer side. Specifically, the final sintered product contains a major amount of the Co_5R single phase on the solid intermetallic phase and up to about 35 percent by weight of the product of a second solid CoR intermetallic phase which is richer in rare earth content than the Co_5R phase.

16 Claims, 2 Drawing Figures

Fig.1.
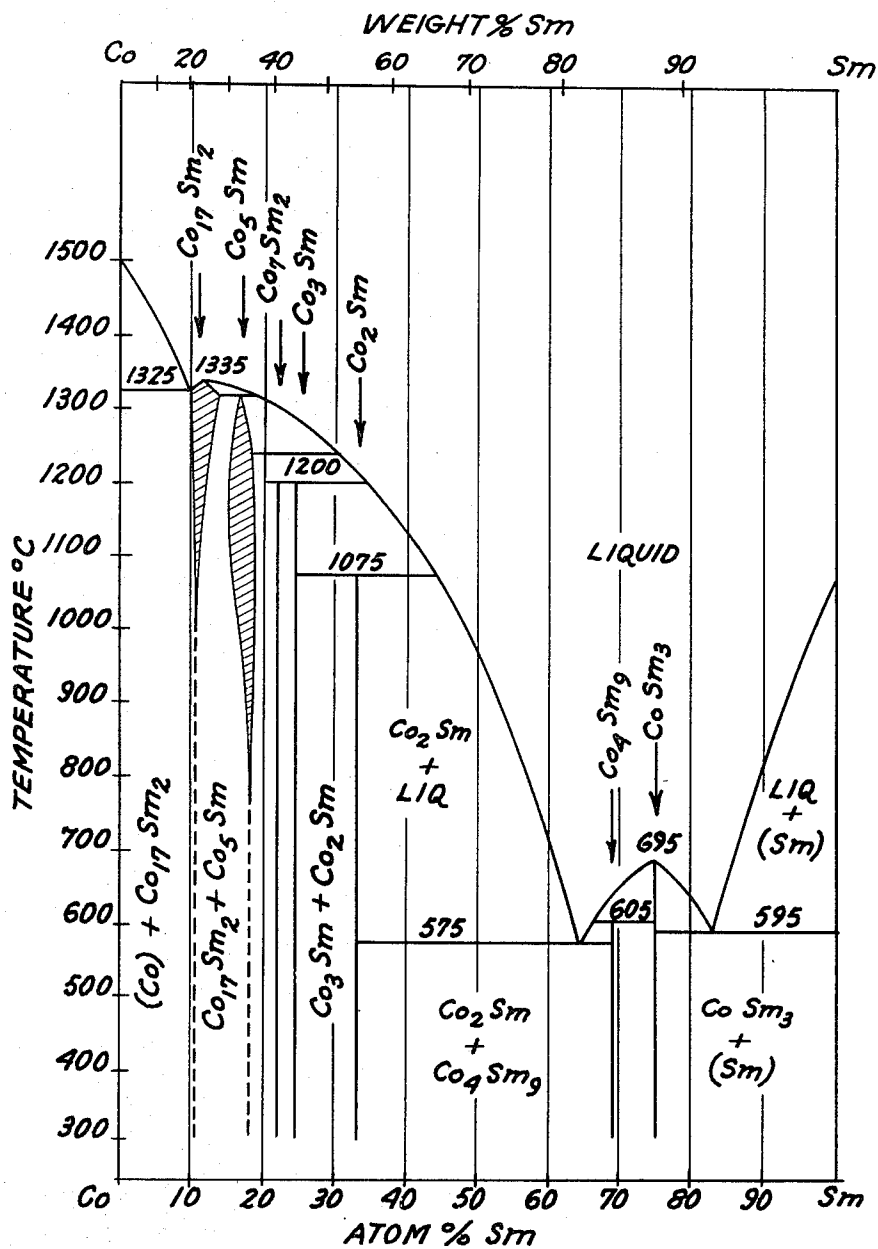
Inventor:
Mark G. Benz,
by Jane M. Binkowski
His Attorney.

Fig. 2.
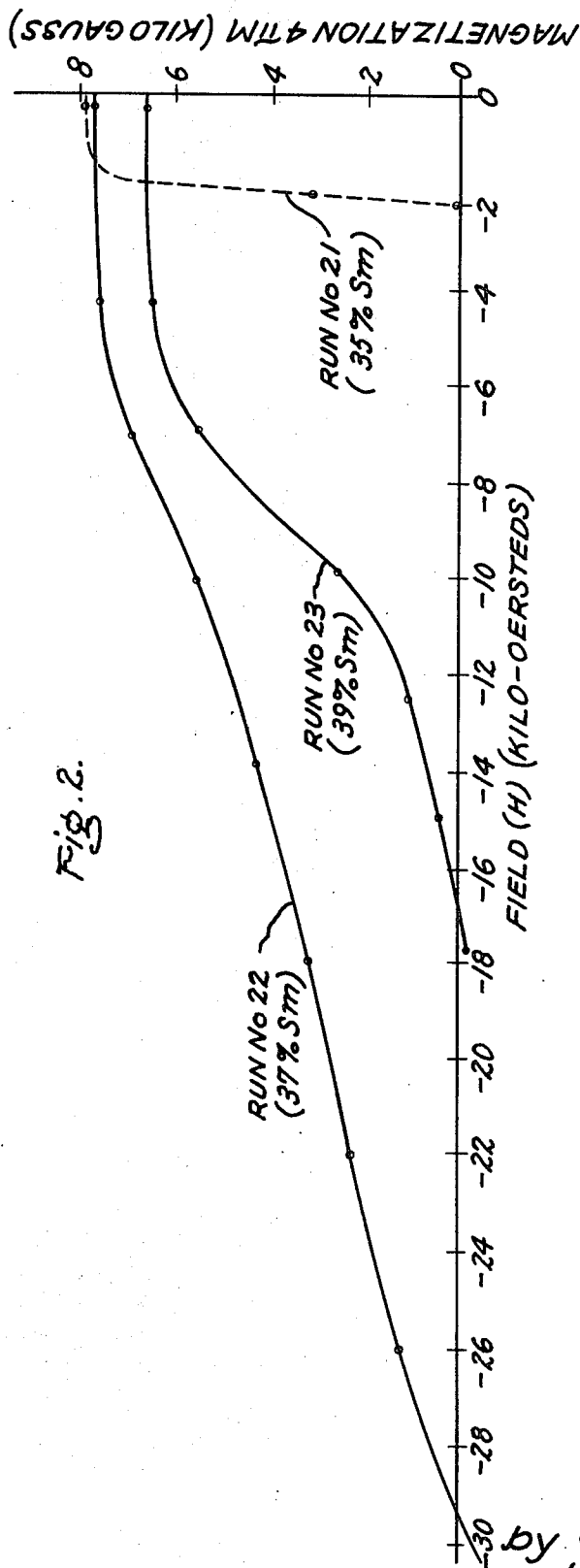
Inventor:
Mark G. Benz,
by Jane M. Binkowski
His Attorney.

PROCESS OF PREPARING LIQUID 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 two produced in accordance with the present invention.

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

The base alloy is one which at sintering temperature exists as a solid Co_5R intermetallic single phase where R is a rare earth metal. The additive cobalt-rare earth alloy is richer in rare earth metal than the base alloy and at sintering temperature it is at least partly in liquid form and thus increases the sintering rate. The base and additive alloys, in particulate form, are each used in an amount to form a mixture which has a cobalt and rare earth metal content substantially corresponding to that of the final desired sintered product.

The mixture is pressed into compacts, preferably in an aligning magnetic field, and sintered to the desired sintered product phase composition and desired density. At sintering temperature, the final sintered product has a composition lying outside the Co_5R single phase region on the rare earth-rich side. Specifically, at sintering temperature, as well as at room temperatures, the final sintered product contains a major amount of the Co_5R solid intermetallic phase and up to about 35 percent by weight of the product of a second CoR intermetallic phase which is richer in rare earth content than Co_5R phase.

The base cobalt-rare earth alloy used in the present process is one which at sintering temperature exists as a Co_5R single intermetallic phase. Since the Co_5R single phase may vary in composition, the base alloy may vary in composition which can be determined from the phase diagram for the particular cobalt-rare earth system, or empirically. For example, FIG. 1 shows that for the cobalt-samarium system, the base alloy at room temperature may vary in samarium content from about

32 to 36 percent by weight since this particular composition is single phase at sintering temperatures ranging from about 950° to 1,200° C. Preferably, for simplicity, the base alloy at room temperature is a Co_5R intermetallic phase.

The additive cobalt-rare earth alloy is one which is richer in rare earth metal content than the base alloy. It must also be one that exists at least partly in a liquid form at sintering temperature. The additive alloy may vary in composition and can be determined from the phase diagram for the particular cobalt-rare earth system or it can be determined empirically. For example, FIG. 1 shows that for the cobalt-samarium system, there are phases which are partly or completely liquid at the temperature ranging from about 950° to 1,200° C. which is a suitable sintering temperature range for Co-Sm in the present process. Any alloy within the range shown in FIG. 1 which forms at least a partly liquid phase at the particular sintering temperature would be a satisfactory additive alloy in the present process. For example, as illustrated in FIG. 1, the Co-Sm additive alloy can vary upward in samarium content from which 46 percent by weight of the additive. If desired, an additive alloy can be empirically selected by a number of methods, such as by means of a composition scan at the sintering temperature, i.e., heating samples of various additive alloy compositions to the desired sintering temperature and observing the extent of the development of the liquid phase.

Although suitable additive CoR alloys fall within a general composition range, the preferred ones are comparatively low in rare earth metal content so that undesirable characteristics of the pure rare earth metal in the additive alloy are minimized. Specifically, for example, pure samarium is both pyrophoric and very ductile and consequently difficult to crush and to blend with the base alloy since it has a tendency to separate out and fall to the bottom of the container. On the other hand, the additive CoSm alloy of samarium content preferably less than 70 percent by weight, is substantially nonreactive at room temperature in air, it can be crushed by conventional techniques, and being slightly magnetic, it clings to the base alloy resulting in a substantially thorough stable mixture. However, as the samarium content of the additive Co-Sm alloy is increased, the additive alloy becomes more reactive and more difficult to blend. On the other hand, the higher the cobalt content of the additive alloy, the stronger are its magnetic properties and the more stable is the particulate mixture it forms with the base alloy.

The rare earth metals useful in forming the present cobalt-rare earth 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, quartenary or which may contain an even greater number of rare earth metals as desired.

Representative of the cobalt-rare earth 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. 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-misch metal, cobalt-cerium-praseodymium, cobalt-yttrium-praseodymium, and cobalt-praseodymium-misch metal.

In carrying out the present process, the base and additive cobalt-rare earth alloys can be formed by a number of methods. For example, each 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 solid base and additive alloys can be converted to particulate form in a conventional manner. Such conversion can be carried out in air at room temperature since the alloys are substantially non-reactive. For example, each alloy can be crushed by mortar and pestle and then pulverized to a finer form by jet milling.

The particle size of the base and additive cobalt-rare earth alloys used in forming the mixture of the present process may vary. Each 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.

In forming the mixture in the present process, the base and additive alloys are each used in an amount so that the resulting mixture has a cobalt and rare earth metal content substantially corresponding to that of the final desired sintered product phase composition. In addition, however, in forming the mixture, the alloy additive should be used in an amount sufficient to promote sintering. This amount depends largely on the specific composition of the alloy additive and can be determined empirically, but generally, the additive alloy should be used in an amount of at least 0.5 percent by weight of the base-additive alloy mixture. Specifically, the larger the rare earth metal component of the additive alloy, the less is the amount of the additive alloy which need be used.

In the present invention, at sintering temperature, the final sintered product should have a phase composition lying outside the Co_5R single phase on the rare earth-rich side. Magnetization of such a product 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 content than the Co_5R phase, a permanent magnet of only inferior magnetic properties can be produced no matter how the magnetization step is carried out.

Specifically, 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 proportionately varying mixtures of base and additive alloys, 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 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.

In carrying out the process of this invention, the base alloy is admixed with the additive alloy in any suitable manner to produce a substantially thorough particulate mixture. The particulate mixture can then 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 mixture is compressed in the presence of an aligning magnetizing field to magnetically align the particles along their easy axis, or if desired, the mixture may 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 40 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 produce 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 mixture 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 component particles. Preferably, sintering is carried out so that the pores in the sintered product are substantially non-interconnecting. A sintered body having a density or packing of at least about 87 percent of theoretical is generally one wherein the pores are substantially non-interconnecting. Such non-interconnectivity is determinable 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 the cobalt-samarium alloy mixture of the present invention, a sintering temperature ranging from about 950° C. and up to about 1,200° C. is suitable with a sintering temperature of 1,100° 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.

The sintered product of the present invention has the appearance of having been liquid sintered. Examination of a polished cross-section of the sintered bulk product under an X-ray microprobe or light microscope shows that its grains differ significantly in appearance from the original particles

5

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, i.e., the appearance is that of a liquid-sintered-smooth surface. In addition, under a light microscope as well as under an X-ray microprobe, there can be seen a material in a number of the pores that appears to have been liquid at high temperatures. Apparently, during sintering, some of the liquid becomes trapped in closing the pores. 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 subjecting 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:

$$\frac{\dfrac{\text{Weight}}{\text{Volume}}}{8.5 \text{ g./cc.}} \times 100 = \text{percent packing}$$

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

The estimated energy product was arrived at from measurements of the open-circuit flux of the sample, its intrinsic coercive force, and its dimensions. On a plot of B vs H, the open-circuit flux point was plotted on a load line corresponding to the sample shape, and the intrinsic coercive force point was drawn on the line B = H in the third quadrant. This point and the open-circuit point were connected with a straight line. The rest of the demagnetization curve was approximated by a

6

straight line from the open-circuit point to the H = O axis with a slope of 45°. The maximum energy product on this line-segment demagnetization curve is the estimated energy product.

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

A base alloy melt and an additive alloy melt of cobalt-samarium were made under purified argon by arc-melting and cast into ingots. The base alloy was formed from 33.3 weight percent samarium and 66.7 weight percent cobalt. The additive alloy was formed from 60 weight percent samarium and 40 weight percent cobalt. Each 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 generally had an average particle size of about 6 microns.

The samples for Run Nos. 1 through 10 were taken from 12 gram mixtures formed by admixing 10 grams of the base alloy powder with 2.14 gram of the additive alloy powder by tumbling to form a substantially thorough mixture composed of 62 weight percent cobalt and 38 weight percent samarium. Since the additive alloy was substantially non-reactive in air and was slightly magnetic, a stable mixture of the two powders was produced. Wet chemical analysis of portions of the mixture showed 37.4 ± 0.3 percent Sm. Portions of the mixture were then compressed into green bodies which were sintered and their magnetic properties determined.

Table 1 tabulates the specific procedure used for each run made. Specifically, in Runs 1 through 10 a portion of the mixture was weighed and then compressed into a circular disc. Compression was carried out in a steel die in an aligning magnetizing field ranging from 7 to 15 kilo-oersteds provided by an iron electromagnet. Each disc was then sintered and its properties determined after sintering. After magnetization at room temperatures in a field of 25 kilo-oersteds, the magnetic properties of the disc were determined.

In Runs 11 through 16, the procedure was substantially the same as in Runs 1 through 10 except that the sample for each run was taken from a master batch formed of 173 grams of the base alloy and 37 grams of the additive alloy to give a mixture composed of 62 weight percent cobalt and 38 weight percent samarium. Specifically, in Runs 11 through 16, each sample was placed in a rubber tube and magnetically aligned therein. For Runs 11 through 13 the aligning magnetizing field was provided by an electromagnet and ranged from 7 to 15 kilo-oersteds. In Runs 14 through 16, the aligning magnetizing field was provided by a superconducting coil which in Runs 14 and 15 was 100 kilo-oersteds and in Run 16 was 60 kilo-oersteds. After magnetic alignment in Runs 11 through 16, the tube was evacuated to freeze the alignment and then it was pressed hydrostatically to form the green body.

The tabulated sintering temperature of 1,050° or 1,100° C. is one at which the additive is in a partly liquid phase.

To prepare the control of Run No. 17, 13.95 grams of the base alloy powder and 0.41 grams of an alloy powder formed from 77 percent by weight cobalt and 23 percent by weight samarium, the alloy powder being the same size and being prepared in the same manner as the base alloy powder, were used to form a mixture of 67 percent by weight cobalt and 33 percent by weight samarium. A portion of the control mixture was placed in a rubber tube and magnetically aligned therein in an aligning magnetizing field of 100 kilo-oersteds provided by a super-conducting coil. The tube was then evacuated to freeze the alignment and then it was pressed hydrostatically to form the green body. The estimated packing of the control before sintering was based on those measured for similar samples prepared in the same manner.

TABLE 1

Runs	Compaction pressures K p.s.i.	Compressed powder disc or green body Size, inches Wt., gms.	Diam.	Thickness or length	Packing, percent	Sintering method Time, hrs.	Temp., °C.	Sintered product Size, inches Wt., gms.	Diam.	Thickness or length	Packing, percent	Magnetic properties of sintered product after magnetization Max. energy prod. (BH)max. (10⁶ gauss×oersteds)	Intrinsic coercive force mHc, K oersteds
1	200	1	0.319	0.115	78.4	1	1,100	1	.3055	.109	90	¹8	−19.7
2	200	2.5	0.507	0.113	79.1	1	1,100	2.5	.482	.108	91	¹8	>−11.6
3	(Product of Run No. 2 sintered longer)					2	1,100	2.5	.480	.106	94	¹8	−15.5
4	(Product of Run No. 3 sintered longer)					3	1,100	2.5	(²)	.1055	(²)	---	−13.5
5	200	2.5	0.507	0.113	79.2	1	1,100	2.5	.484	.1075	91	¹7.5	−20.8
6	(Product of Run No. 5 sintered longer)					2	1,100	2.5	.482	.105	94	¹7.5	−19.2
7	200	2.5	0.508	0.111	82.2	1	1,100	2.5	.485	.105	93	¹8	−20.0
8	200	2.5	0.507	0.111	80.1	½	1,100	2.5	.483	.106	93	¹7.5	−17.5
9	200	2.5	0.507	0.114	78.0	15	1,050	2.5	.496	.1115	83	¹7.5	−20.8
10	200	2.5	0.505	0.113	79.3	½	1,100	2.5	.484	.108	90	¹8	−21.0
11	196	8.32	0.277	1.23	80.5	½	1,100	8.319	.268	1.15	92	15	>−12
12	196	5.98	0.251	1.074	81	½	1,100	5.966	.241	1.029	91.4	10.8	>−12
13	60	7.24	0.318	1.1	41	1½	1,100	7.24	.2815	.995	83	13.4	>−12
14	200	(Did not measure)				2	1,100	(Did not measure)			---	---	−15.2
15	200	6.42	0.249	1.16	81.6	½	1,100	0.42	.241	1.11	91	14.8	>−12
16	200	6.92	0.249	1.25	81.6	½	1,100	6.92	.242	1.196	90	16	>−12
17³	200	(Did not measure)			¹81	½	1,100	6.73	.265	1.055	83	6	−1.7

¹ Estimate.
² Sample broken.
³ Control.

Table I shows that sintering of the green body produces a sintered product which weighs about the same as the green body indicating no loss in the cobalt and samarium components. However, the green body does undergo some shrinkage during sintering as illustrated by the packing of the sintered product which was significantly higher in every run than that of the green body. In Runs 1 through 10 the energy product was estimated due to the geometric limitations of the product.

Runs Nos. 1 through 16 specifically illustrate the significantly better magnetic properties obtained by present process as compared to Run No. 17, the control, where no additive alloy of the present invention was used.

Examination of the sintered products of Run Nos. 5 and 16, by standard metallographic analysis showed that two phases were present in each product. Micrographs of a polished cross-section of each product showed that the pores were substantially non-interconnecting and that a major amount of one phase was present along with a minor amount of a second phase and that traces of a few other phases also appeared to be present. In addition, under a light microscope as well as under an X-ray microprobe, there can be seen material deposits in a number of the pores that appear to have been liquid at high temperatures. Also, substantially all of the grains of each sintered product were rounded and had a smooth surface which appeared to be a liquid sintered smooth surface. The average grain size of each sintered product was about 7 microns.

Examination of a polished cross-section of the sintered product of Run No. 17, the control, by standard metallographic analysis showed only a single intermetallic phase. Standard wet chemical analysis of the control showed it to contain 33 percent by weight samarium.

After aging the sintered product of Run No. 1 for 400 hours at a temperature of 150° C. in air, its intrinsic coercive force was determined and found to be unchanged. This illustrates the highly stable properties of the permanent magnets of the present invention.

EXAMPLE 2

In this example the stability of magnetic properties of the sintered product of Example 1 was determined.

The sintered product of Run No. 14 of Example 1 had an intrinsic coercive force of 15,200 oersteds. This product was used to provide the particulate samples of the present example. Initially, the product was crushed to a particle size ranging from 210 to 420 microns by mortar and pestle. The coercive force of a portion of this crushed material was determined. A second portion of the crushed material was placed in air in an oven at a temperature of 150° C. for 17 hours. Its coercive force was then determined and the results are shown in Run No. 18 in Table II.

For Run No. 19 of Table II, the remaining portion of the crushed material was further crushed in the same manner to produce a powder ranging in size from 42 to 210 microns, and the same procedure was then followed as in Run No. 18.

For Run No. 20 the remaining material was crushed to a size less than 42 microns and again the same procedure was followed as in Run No. 18.

In all of the runs of Table II, the intrinsic coercive force of the sintered cobalt-rare earth powder, was measured at room temperature in the same manner. Specifically, a specimen of the powder was prepared for magnetic measurement by introducing it into a body of molten paraffin wax in a small glass tube and cooling the wax in an aligning magnetic field of about 17,500 oersteds until the paraffin solidified. The intrinsic coercive force of each such prepared sample was then measured after magnetization in a field of 17,500 oersteds. The results are shown in Table II.

TABLE II

Run No.	Sintered Product Particle Size, Microns	Intrinsic Coercive Force (mHc, Koe.) As Crushed	Intrinsic Coercive Force (mHc, Koe.) After 17 hours. at 150°C in Air
18	210 – 420	14.2	14.2
19	42 – 210	11.5	10.0
20	<42	11.5	8.2

Table II illustrates the good stability of the permanent magnet materials produced by the present process. Specifically, after extensive heat aging in air, Run No. 18 showed no change in coercive force and Run No. 19 showed a very small loss in coercive force. Run No. 20 shows some loss in coercive force and indicates that very small particle size material has less stable magnetic properties.

The sintered particulate material of Table II is particularly suitable for magnetic alignment and matrix bonding to give a stable permanent magnet.

EXAMPLE 3

In this example the magnetic properties of sintered products formed from three different cobalt-samarium mixtures were determined.

9

Portions of the base alloy (66.7 percent by weight cobalt and 33.3 percent by weight samarium) powder and the additive alloy (40 percent by weight cobalt and 60 percent by weight samarium) powder disclosed in Example 1 were used to prepare the three mixtures of this example. Specifically, for Run No. 21, 13.12 grams of the base alloy were admixed with 0.88 grams of the additive alloy to form a mixture composed of 65 percent by weight cobalt and 35 percent by weight samarium. For Run No. 22, 12.08 grams of the base alloy were admixed with 1.92 grams of the additive alloy to form a mixture composed of 63 percent by weight cobalt and 37 percent by weight samarium. For Run No. 23, 11.04 grams of the base alloy were admixed with 2.96 grams of the additive alloy to form a mixture composed of 61 percent by weight cobalt and 39 percent by weight samarium. Each mixture was formed in the same manner and into substantially the same sized bar as disclosed for Run No. 11 of Example 1. Each bar was sintered at a temperature of 1,100° C. for one-half hour. The packing of Run No. 21 (35% Sm) was 84 percent, of Run No. 22 (37% Sm) 89 percent and of Run No. 23 (39% Sm) 87 percent. Each bar was magnetized at room temperatures in a field of 100 kilo-oersteds. Each bar was then demagnetized using the specific magnetizing fields shown in FIG. 2 and its magnetization $4\pi M$ in such field was determined. Since none of the sintered bars showed a weight loss, its cobalt and samarium content was the same as the mixture it was formed from.

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 kilogauss. From the demagnetization curves of FIG. 2, it can be seen that the product of Run No. 22 containing 37 percent 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 1,100° C. as well as at room temperature is comprised of a major amount of the Co_5Sm single intermetallic phase, i.e., about 95 percent by weight of the product, and a minor amount of the Co_7Sm_2 phase, i.e., about 5 percent by weight of the product. X-ray diffraction analysis of this product showed it to have two phases.

FIG. 2 shows poor magnetic properties for the sintered product of Run No. 21 composed of 65 percent cobalt and 35 percent by weight samarium which according to FIG. 1 is the composition for a single intermetallic phase. Microscopic analysis of the product of Run No. 21 showed it to be a single phase.

EXAMPLE 4

In this example, the procedure and materials used were substantially the same as that set forth in Example 1 for preparing the compressed disc of Run No. 1 and a number of sintering runs were carried out in substantially the same manner as Run No. 1 of Example 1.

Standard wet chemical analysis of the initial powder cobalt-samarium mixture as well as the sintered product of each run showed that the sintered products contained the same amount of samarium by weight as the starting powder.

EXAMPLE 5

In this example, a permanent magnet was formed comprised of the sintered powder of the present invention distributed in a metal matrix.

In order to produce a thorough mixture, the sintered powder of Run No. 18 of Example 2 was initially demagnetized by heating it to a temperature of 900° C. for 10 minutes. The demagnetized powder was then mixed with a −100 mesh (U.S. Standard Screen Size) aluminum powder to produce a mixture of 80 volume percent of the sintered powder and 20 volume percent of the aluminum powder.

A slurry of the mixture was made with isopropyl alcohol and placed in a die press in an aligning magnetizing field of 15 kilo-oersteds and pressed under a pressure of 200 K psi. The resulting compressed body had a diameter of 0.336 inch and a length of 0.351 inch. After it was magnetized in a field of 15

10

kilo-oersteds, the resulting magnet had an open circuit induction B_o of 2395 gauss.

EXAMPLE 6

A base alloy melt and an additive alloy melt were formed under purified argon by arc-melting and were cast into ingots. The base alloy was formed from 68 weight percent cobalt, 16 weight percent samarium and 16 weight percent cerium-misch metal. The additive alloy was formed from 40.8 weight percent cobalt and 59.2 weight percent samarium. Each ingot was formed into a powder in the same manner as disclosed as in Example 1 ranging in size from approximately 1 to about 10 microns in diameter with an average particle size of about 6 microns.

24.48 grams of the base alloy were admixed with 5.51 grams of the additive alloy by tumbling to form a substantially thorough mixture of 63 weight percent cobalt and 37 weight percent rare earth.

7.83 grams of the mixture were aligned in an aligning magnetic field of 60 kilo-oersteds and then compressed under a pressure of 200 K psi. to form a bar which was 0.288 inch in diameter and 1.075 inches long and had a packing of 79 percent. The bar was sintered for one-half hour at a temperature of 1,050° C. Upon completion of the sintering, the sintered bar had a 0.284 inch diameter and a length of 1.020 inches and a packing of 87 percent. It also weighed 7.83 grams which indicates that none of the material was lost during sintering. After the sintered bar was magnetized in a field of 16.5 kilo-oersteds, it had an intrinsic coercive force $_mH_c$ of 4,600 oersteds and an open circuit induction B_o of 6160 gauss in a self-demagnetizing field of −300 oersteds.

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 on 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 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.

In copending U.S. Patent application Ser. No. 33,348 entitled "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 cobalt-rare earth metal alloy which 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, compacting the alloy particles to produce a green body, and sintering the green body to produce a sintered body containing a major amount of Co_5R phase 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.

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

11

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.

What is claimed is:

1. A process for producing a sintered cobalt-rare earth intermetallic product containing a Co_5R intermetallic phase and a CoR intermetallic phase which is richer in rare earth metal content than said Co_5R intermetallic phase which comprises providing a particulate mixture of a base cobalt-rare earth metal alloy and an additive cobalt-rare earth metal alloy, said base alloy existing at sintering temperature as a solid Co_5R intermetallic phase and said additive CoR alloy existing at sintering temperature as at least a partly liquid phase, said base alloy and said additive alloy each being used to form a mixture which has a cobalt and rare earth metal content substantially corresponding to that of the final sintered product with said additive CoR alloy being present in an amount of at least 0.5 percent by weight of said mixture, pressing said mixture 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 80 percent of theoretical and containing the Co_5R intermetallic phase in an amount of at least 65 percent by weight of said product and a second CoR intermetallic phase which is richer in rare earth metal content than said Co_5R phase in an amount of up to about 35 percent by weight of said 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 cobalt-rare earth alloys are cobalt-samarium alloys.

3. A process according to claim 2 wherein said base alloy ranges in samarium content from about 32 to 36 percent by weight.

12

4. A process according to claim 3 wherein said base alloy is substantially Co_5Sm.

5. A process according to claim 2 wherein said additive alloy ranges in samarium content from about 46 percent to about 65 percent by weight of said additive.

6. A process according to claim 2 wherein said mixture is composed of about 62 percent by weight cobalt and 38 percent by weight samarium.

7. A process according to claim 2 wherein said sintering temperature ranges from about 950° C. to about 1,200° C.

8. A process according to claim 1 wherein said base cobalt-rare earth alloy is a cobalt-samarium-cerium mischmetal alloy.

9. A process according to claim 1 wherein said pressing of said mixture into a green body is carried out in an aligning magnetizing field.

10. A process according to claim 1 wherein said sintered product has a density of at least about 87 percent of theoretical.

11. A process according to claim 1 wherein the particle size of said particulate mixture ranges from about 1 to 10 microns.

12. 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.

13. A process according to claim 12 wherein R is samarium.

14. 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.

15. 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.

16. A process according to claim 14 which includes the step of subjecting said bonded particles in said matrix material to a magnetizing field to magnetize said particles.

* * * * *

5

10

15

20

25

30

35

40

45

50

55

60

65

70

75