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RARE EARTH INTERMETALLIC COMPOUNDS CONTAINING CALCIUM

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No Drawing. Application Aug. 16, 1971, Ser. No. 172,290, now Patent No. 3,748,193, which is a continuation-in-part of abandoned application Ser. No. 849,875, Aug. 13, 1969. Divided and this application Dec. 18, 1972, Ser. No. 315,813
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U.S. Cl. 148—31.57 1 Claim

ABSTRACT OF THE DISCLOSURE

A reduction-diffusion process for producing novel rare earth intermetallic compounds, for example, cobalt-rare earth intermetallic compounds, especially compounds useful in preparing permanent magnets. A particulate mixture of rare earth metal oxide, cobalt and calcium hydride is heated to effect reduction of the rare earth metal oxide and to diffuse the resulting rare earth metal into the cobalt to form the intermetallic compound.

This is a division of application Ser. No. 172,290, filed Aug. 16, 1971, now Pat. No. 3,748,193, which is a continuation of Applicant's then copending application Ser. No. 849,875 filed Aug. 13, 1969, now abandoned, and all assigned to the same assignee.

The present invention relates to rare earth intermetallic compounds, permanent magnets and a reduction-diffusion process for preparing the compounds.

Permanent magnets, i.e. "hard" magnetic materials, 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. A number of cobalt-rare earth intermetallic compounds, as for example Co_5Sm, can be made into permanent magnets. However, these intermetallic compounds are not widely used in forming permanent magnets because the methods of preparing these compounds are lengthy, time-consuming and costly. For example, a conventional process for preparing a cobalt-samarium intermetallic compound useful as a permanent magnet comprises reduction of the samarium oxide by a number of techniques such as heating the oxide with lanthanum metal chips in a high temperature vacuum retort. On heating in vacuum the samarium is reduced and, being more volatile than lanthanum, is vaporized from the retort and condensed in the cold zone where it later must be chipped off the walls of the retort. This recovered bulk samarium metal is suitable only for melting stock which is admixed with molten cobalt in proper amount and cast into an ingot. The ingot is then ground to a fine particle size, ordinarily finer than one micron, to develop its permanent magnet properties. The ground material may then be compressed in a magnetizing field and sintered to form a solid magnet. A flexible magnet may be formed by incorporating the ground material in a magnetizing field in a matrix of an elastomer or polymer.

It is an object of the present invention to produce rare earth intermetallic compounds by a reduction process which avoids the time-consuming, costly steps of conventional processes.

I have discovered that the cobalt-rare earth intermetallic compounds can be prepared directly from rare earth metal oxide and cobalt powder. This process eliminates the necessity of the separate steps of past processes of forming the rare earth bulk metal product by a process requiring the use of costly lanthanum metal as a reducing agent. In addition, such steps as melting the samarium with the cobalt, casting the melt into an ingot and grinding the ingot to a fine particle size are also eliminated.

Briefly stated, the process of the present invention comprises heating a particulate mixture of a rare earth metal oxide, cobalt and calcium hydride to effect reduction of the oxide and to diffuse the resulting rare earth metal into the cobalt to form the intermetallic compound.

One advantage of the present process is that the particle size of the cobalt-rare earth intermetallic compound produced is predeterminable because it is nearly the same as the particle size of the cobalt particles initially used. Since cobalt powder is presently commercially available in a wide range of particle sizes and size distributions, the present process is useful to produce cobalt-rare earth intermetallic compound in a corresponding wide range of particle sizes and size distributions. This is in contrast to past processes where the cobalt-rare earth intermetallic compound must be ground to particle size since grinding does not provide direct control over the actual particle size, or particle size distribution, and must be followed by a time-consuming screening procedure to recover particles of the desired size. Another advantage of the present process is that the particles of cobalt-rare earth intermetallic compound produced are substantially free of strain whereas the particles produced by grinding procedures of past processes are inherently strained.

Still another advantage of the present process is that since it is useful to produce large particles as well as small particles of controlled size, a desired amount of each particle size can be admixed and compressed to form a more dense body since the small particles will fill the interstices between the large particles. Sintering of the more dense body results in a more dense magnetic material with correspondingly improved magnetic properties.

Considering the process of this invention in more detail, the following equation represents the stoichiometric reaction for forming Co_5R, where R is a rare earth metal, by the reduction of the rare earth from the oxide to a constituent of the cobalt intermetallic compound using samarium as an example:

$$5\,Co + 1/2\,Sm_2O_3 + 3/2\,CaH_2 \xrightarrow{heat} Co_5Sm + 3/2\,CaO + 3/2\,H_2$$

Substantially stoichiometric amounts of the active constituents, cobalt, the rare earth metal oxide and calcium hydride, for preparing the cobalt-rare earth intermetallic compound are satisfactory in the present process. However, under certain operating conditions, an excess amount of the rare earth metal oxide may be used to cover any losses of the rare earth metal. In addition, preferably, an amount of calcium hydride in excess of the stoichiometric amount necessary to reduce the rare earth metal oxide is used so that the excess calcium hydride is converted to metallic calcium which precipitates at the boundaries of the particles of the resulting cobalt-rare earth intermetallic compound. The resulting product mass can then be placed in air or other oxygen and moisture-containing atmosphere to allow the precipitated calcium to oxidize whereupon it undergoes a change in volume sufficient to disintegrate the mass and release the particles of the cobalt-rare earth intermetallic compound.

The rare earth metal oxide can vary in particle size. It is usually available in commerce in precipitated form, which is the preferred form herein since this form is a very fine particle size, i.e. of the order of 0.1 micron and highly pure. The smaller the particle size, the faster the oxide is reduced, and the resulting rare earth metal is thereby made available for diffusion into the cobalt in a shorter period of time.

The oxides of the rare earth metals useful in the present process are those of the rare earth metals which are the 15 elements of the lanthanide series having atomic num-

bers 57 to 71 inclusive. The element yttrium (atomic number 39) is commonly found with and included in this group of metals and, in this disclosure, is considered a rare earth metal. Mixtures of rare earth metal oxides can also be used. Representative of the oxides useful in the present invention are samarium oxide (Sm_2O_3), yttrium oxide (Y_2O_3) and misch metal oxides (M_2O_3), mesch metal being 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.

The cobalt can be used in a wide range of particle size and is available commercially in such form. The finer sized particles, i.e. about one micron or less, are preferred since their smaller size allows a faster rate of formation of the desired intermetallic compound. In addition, since the size of the intermetallic compound is essentially the same as that of the initial cobalt particles, the finer sized cobalt is preferred because the maximum coercive force obtainable is higher. Specifically, the coercive force varies inversely with the particle size of the intermetallic compound used in forming the permanent magnet. On the other hand, the coarser the cobalt particles, the longer is the period of time required to carry out the diffusion of the rare earth metal to form the compound, and also, the maximum coercive force obtainable is diminished. For most permanent magnet applications, the size of the cobalt particles may range up to about 100 mesh.

Since the calcium hydride decomposes in the present process, it may vary widely in particle size and may be as coarse as 12 mesh or coarser. Generally, a pulverized powder is preferred so that an intimate mixture of the active constituents can be produced. Commercially available calcium hydride always contains some calcium oxide. This will not interfere with proper operation of the process so long as there is a sufficient amount of calcium hydride to reduce the rare earth metal oxide as well as cobalt oxide if cobalt is introduced in that form. The necessary excess amount of commercial calcium hydride needed is determinable empirically.

A number of conventional techniques can be used to carry out the instant process. Preferably, the cobalt, calcium hydride and rare earth metal oxide are thoroughly mixed so that in carrying out the reaction, the calcium hydride, which is the reducing agent, can act on the oxide effectively, and also, so that the resulting rare earth metal can readily diffuse into the cobalt particles. In grinding calcium hydride, if any grinding is required, and in handling the powder mixture, it is essential to use protective enclosures so that the atmosphere may be maintained completely free of moisture. While calcium hydride is substantially inert in completely dry air, the powder or dust is highly explosive under conditions where an electrostatic discharge might occur. Therefore, for safety considerations a protective atmosphere such as a nitrogen atmosphere is preferable to air for mixing and handling the powder. To prevent contamination, the loose powder mixture is preferably placed in a metal foil bag, e.g., molybdenum or iron metal foil, or a self-supporting metal pan having a close-fitting cover. Alternatively, the loose powder can first be pressed into bricks to decrease the volume per unit weight of material, thereby increasing the furnace throughput.

The mixture of active constituents is initially heated to decompose the calcium hydride and reduce the rare earth oxide. Such initial heating should be carried out in an inert atmosphere such as, for example, argon or helium or a partial vacuum. It can also be carried out in an atmosphere of hydrogen since hydrogen is evolved at this time. In addition, since hydrogen gas is evolved, this heating can be carried out at atmospheric pressure. Specifically, at about atmospheric pressure when a temperature of about 850° C. is attained, the reduction process begins as indicated by the evolution of hydrogen and it continues to evolve up to a temperature of about 1000° C. Substantially all the rare earth metal oxide is reduced under these conditions. To carry out the diffusion of the resulting rare earth metal, heating is then continued in hydrogen or an inert atmosphere such as, for example, argon or helium or a partial vacuum. Specifically, to carry out the diffusion, heating is maintained long enough at a temperature which allows the resulting rare earth metal to diffuse into the cobalt to form the desired intermetallic compound. This diffusion heating period and the diffusion heating temperature depend largely on the rare earth metal to be diffused and the size of the cobalt particles. This is determinable empirically. For example, in a substantial vacuum, it takes about an hour at a temperature of about 1050 to 1100° C. for samarium to diffuse into cobalt of particle size from 1 to 5 microns. For cobalt powder having a particle size of 10–20 microns, about 4 hours in a substantial vacuum at a temperature of 1050–1100° C. is sufficient to accomplish the samarium diffusion. Coarser cobalt particles require correspondingly longer diffusion heating periods or higher diffusion temperatures.

The product of the present invention can be cooled in an inert atmosphere such as helium or argon or in a vacuum. Where a substantially stoichiometric amount of calicum hydride is used, the product is generally a fused cake which requires grinding to form a flowable material. Where excess calcium hydride is used, however, the precipitated metallic calcium, which is allowed to oxidize, will generally disintegrate in excess of 90% of the product to a flowable particulate material. Some minor amount of grinding might be necessary to completely disintegrate the product or produce it in a finer form.

To recover the cobalt-rare earth compound particles, a variety of separation techniques can be employed. In one technique a magnetic separator can be used to attract the cobalt intermetallic compound particles, leaving the calcium oxide. In another method, water is added to the particulate product to convert the calcium oxide to calcium hydroxide which is a flocculate precipitate that can be effectively decanted off with repeated washings with water. A preferred final cleanup treatment comprises admixing dilute acetic acid with the recovered cobalt intermetallic compound particles to leach away traces of remaining calcium hydroxide. The cobalt-rare earth intermetallic compound particles can then be rinsed with water and dried in a conventional manner.

In the present process, if desired, the calcium hydride can be formed in situ by a number of methods. One method comprises admixing calcium carbide with the rare earth metal oxide and cobalt and heating the mixture in the presence of hydrogen to form the calcium hydride. In another method magnesium chips or powder are admixed with calcium oxide and heated in hydrogen to form calcium hydride and magnesium oxide which ran remain in the mixture until completion of the process. Once the calcium hydride is formed in situ, the process then can proceed in the same manner as if calcium hydride had been added initially.

In one embodiment of the present invention, the rare earth metal oxide is initially admixed with the calcium hydride to affect reduction of the rare earth metal constituent. Specifically, using samarium oxide as an example, the samarium oxide powder is admixed with calcium hydride, and the mixture is then heated to affect reduction of the rare earth metal constituent. Specifically, the stoichiometric reaction for this embodiment is as follows:

$$Sm_2O_3 + 3CaH_2 \xrightarrow{\Delta} 2Sm + 3CaO + 3H_2.$$

The resulting cake mixture can be ground and then admixed with cobalt particles and heated to diffuse the samarium into the cobalt to form the intermetallic compound which can then be separated from the calcium oxide as already disclosed.

In another embodiment of the present invention, cobalt oxide instead of metallic cobalt powder can be used. Under these circumstances, an additional quantity of calcium hydride should be added to the mixture of rare earth metal oxide, cobalt oxide and calcium hydride to affect reduction of cobalt oxide to metallic cobalt. The stoichiometric reaction describing the reduction of the cobalt oxide is as follows:

$$CoO + CaH_2 \xrightarrow{\Delta} Co + CaO + H_2.$$

In still another embodiment of the present process, cobalt oxide instead of metallic cobalt, is initially mixed with the rare earth metal oxide alone and the mixture is heated in hydrogen or other reducing atmosphere to reduce the cobalt oxide to metallic cobalt. The reaction is as follows:

$$CoO \text{ (dispersed in rare earth metal oxide)} + H_2 \xrightarrow{\Delta}$$

$$Co \text{ (dispersed in rare earth metal oxide)} + H_2O.$$

The resulting mixture is admixed with particulate calcium hydride and then heated, as disclosed, to carry out the reduction of the rare earth metal oxide and the diffusion of the resulting rare earth metal into the cobalt.

The present process is also useful in forming cobalt-rare earth intermetallic compounds other than Co_5R, where R is a rare earth metal, merely by using the proper amounts of the active constituents. In addition, a cobalt-rare earth intermetallic compound having a smaller amount of rare earth than Co_5R, can be used in the present process along with proper amounts of the active constituents to produce Co_5R.

In still another embodiment of the present invention, alloys of cobalt with other ferromagnetic metals or mixtures of cobalt with other ferromagnetic metals may be used instead of or in addition to the cobalt. Representative of such materials are alloys of cobalt and iron or mixtures of cobalt and iron; alloys or mixtures of cobalt, iron and manganese; and alloys or mixtures of cobalt and manganese. Likewise, oxides of alloys of cobalt and other ferromagnetic metals, or mixtures of oxides of cobalt and other ferromagnetic metals instead of, or in addition to the cobalt oxide can be used in the present invention. Typical of these materials are oxides of cobalt and iron alloys or mixtures of oxides of cobalt and iron; oxides of alloys or mixtures of cobalt, iron and manganese; and oxides of alloys or mixtures of cobalt and manganese.

In another embodiment of the present invention, iron can be used instead of cobalt to produce the iron-rare earth intermetallic compound desired. Likewise, iron oxide (Fe_2O_3) can be used in the same manner as cobalt oxide in the present invention to produce iron-rare earth intermetallic compounds. In addition, alloys or mixtures of iron with other ferromagnetic metals, or oxides of alloys or mixtures of iron with other ferromagnetic metals can also be used such as, for example, alloys or mixtures of iron and manganese or their oxides.

All parts and percentages used herein are by weight unless otherwise noted and where screen size is referred to, it is the U.S. Standard Screen Size.

The invention is further illustrated by the following examples.

EXAMPLE 1

In this example, in preparing the formulation, a quantity adjustment factor of 0.07299 was used. The formulation was as follows:

Cobalt powder (Sherritt Gordon, Ltd. Grade NF–1 micron)=58.89 (At. wt. Co)×10 g. moles×0.07299=42.984 g.

Sm_2O_3 (precipitated, 99.9% pure)=348.86 (mol. wt. Sm_2O_3)×0.07299=25.46 grams.

Calcium Hydride (14 mesh)=42.1 (mol. wt. CaH_2)×3 g. moles×2 (2×stoichiometric req.)×0.07299=18.4362 g.

The constituents of the formulation were placed in a plastic bag under a nitrogen atmosphere and blended manually until a thoroughly blended mixture was obtained. The mixture was then placed in a tantalum foil lined molybdenum foil container which was then placed in a clear fused silica tube and inserted in an air-atmosphere tube furnace. The tube was evacuated at room temperature and filled with hydrogen gas which was maintained at ⅔ atmosphere.

The container was then heated and when a temperature of about 850° C. was obtained, hydrogen gas evolved and was bled off so that ⅔ atmosphere of hydrogen gas was maintained. When a temperature of 1000° C. was obtained, hydrogen gas ceased to evolve, and at this temperature, the atmosphere was gradually decreased to a vacuum, and heating at a temperature of 1000° C. was then continued in a vacuum for 30 minutes to carry out the diffusion of the samarium. The product was then allowed to cool to room temperature in the vacuum. The product was a solid mass which was placed in air at room temperature for 96 hours during which period it de-agglomerated to a flowable particulate material due to the oxidation of excess metallic calcium. The particle size was about 10% greater in diameter than that of the initial cobalt particle size. A portion of this product was formed into a specimen for determination of intrinsic coercive force. Specifically, a sample of the cobalt-rare earth intermetallic powder was prepared for magnetic measurement by mixing it with a small amount of catalyzed epoxy resin (sold under the Trademark Calignum) sufficient to bind it and the mixture was placed in a cylindrical non-magnetic foil having one closed end, a 5/16 inch diameter and a length of about ½ inch. The resin was then allowed to harden while the specimen was maintained in an aligning magnetic field of 10,000 oersteds. The intrinsic coercive force of each such prepared sample was then measured at room temperature after magnetization in a field of 100,000 oersteds. The specimen was found to have an intrinsic coercive force H_{ci} of 35,825 oersteds.

The remaining portion of the product was ground by ball-milling for one hour to form a finer material. The resulting powder mixture was mixed with water to convert calcium oxide to a flocculant precipitate of $Ca(OH)_2$. The $Ca(OH)_2$ was then removed by repeated washes in water and the residual calcium hydroxide dissolved by a final wash with dilute acetic acid. The powder was then washed with water, alcohol and acetone, and dried under vacuum. The product powder particle size after ball-milling was smaller than that of the initial cobalt particle size.

A portion of the dried powder product was subjected to standard chemical analysis and was found to contain 66.4% by weight cobalt, 33.7% by weight samarium and 0.07% by weight calcium. A portion of the dried product was also subjected to X-ray analysis and was found to be comprised of single phase Co_5Sm intermetallic compound. Another portion of this powder product was doped by adding 4.5 weight percent samarium hydride ground powder and pressed into a 5/16" diameter cylindrical magnet at 120,000 p.s.i. in an aligning magnetic field of 18,000 oersteds. It was then densified by sintering at 1100° C. for 4 hours in a calcium-gettered helium atmosphere. After magnetizing at 100,000 oersteds the magnet showed B_r=6600 g., H_c=6050 oersteds, H_{ci}=26,000 oersteds, and $BH_{max.}=9.9\times10^6$ gauss-oersteds energy product.

EXAMPLE 2

In this example, in preparing the formulation, a quantity adjustment factor of 0.12 was used. The formulation was as follows:

Cobalt powder (Sherritt Gordon, Ltd., Grade SF–400, 10–20 microns)=58.89 (At. wt. Co)×10 g. moles×0.12 =70.67 g.

Sm_2O_3 (precipitated, 99.9% pure)=348.86 (mol. wt. Sm_2O_3)×0.12=41.863 g.

Calcium Hydride (14 mesh)=42.1 (mol. wt. CaH_2)×3 g. moles×1.81 (1.81×stoichiometric req.)×0.12=27.44 g.

The constituents of the formulation were placed in a plastic bag under a nitrogen atmosphere and blended manually until a thoroughly blended mixture was obtainend. The mixture was then placed in a tantalum foil lined molybdenum foil container which was then placed in a clear fused silica tube and inserted in an air atmosphere tube furnace. The tube was evacuated at room temperature, heated to 200° C. under vacuum and then filled with hydrogen gas which was maintained at one atmosphere.

The heating was continued and when a temperature of about 850° C. was obtained, hydrogen gas evolved and was bled off so that one atmosphere of hydrogen gas was maintained. When a temperature of 1000° C. was obtained, hydrogen gas ceased to evolve. Heating was continued in hydrogen until a temperature of 1100° C. was reached and then continued at that temperature in hydrogen for 2 hours followed by 2 hours of continued heating at a pressure of ⅓ atmosphere to carry out the diffusion of the samarium into the cobalt. The system was then evacuated by a mechanical vacuum pump to a pressurue of approximately 100 microns of Hg and the product was allowed to cool under this vacuum to room temperature. The product was a solid mass which was placed in air at room temperature for 96 hours during which period it de-agglomerated to a flowable particulate material due to the oxidation of excess metallic calcium. The particle size was about 10% greater in diameter size than the initial cobelt particle size. The product was ball-milled for one hour to produce a finer material. The resulting powder mixture was mixed with water to convert calcium oxide to a flocculant precipitate of $Ca(OH)_2$. The $Ca(OH)_2$ was then removed by repeated washes in water and the residual calcium hydroxide dissolved by a final wash with dilute acetic acid. The powder was then washed with water, alcohol, and acetone, and dried under vacuum. The product powder particle size after ball-milling was smaller than that of the initial cobalt particle size.

A portion of the dried powder product was subjected to standard chemical analysis and was found to contain 66.6% by weight cobalt, 33.1% by weight samarium and 0.20% by weight calcium.

The coercive force of a portion of the washed and dried powder was determined in the same manner as disclosed in Example 1 except that, instead of 100,000 oersteds, a magnetizing field of 30,000 oersteds was used. The specimen was found to have an intrinsic coercive force of 8000 oersteds.

A permanent magnet was prepared by pressing aportion of the washed and dried powder at 120,000 p.s.i. in a magnetic field of 18,000 oersteds. The pressed pellet was placed in a close fitting tantalum foil holder and samarium chips comprising 2.8% of the specimen weight were placed on top of the specimen. A tantalum foil cover was then placed on the holder and the assembly heated to 1050° C. in a calcium-gettered helium atmosphere furnace and held at temperature for 15 minutes. After removal from the furnace it was noted that the samarium metal chips had infiltrated the pressed powder body, converting the whole to a mechanically sound body. The body was magnetized at 30,000 oersteds and found to have a residual magnetic field density of 1950 gauss and to possess an intrinsic coercive force of 15,500 oersteds.

What I claim as new and desire to secure by Letters Patent of the United States is:

1. A magnetic intermetallic compound in particulate form and substantially free of strain, said compound being of a rare earth metal and a member selected from the group consisting of cobalt, iron, alloys of cobalt and iron, a lloys of cobalt, iron and manganese and alloys of cobalt and manganese, said compound containing calcium in an amount ranging from about 0.07% by weight to 0.2% by weight.

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