

[54]	RARE EARTH INTERMETALLIC COMPOUNDS PRODUCED BY A REDUCTION-DIFFUSION PROCESS	3,639,181	2/1972	Cech.....	148/100
		3,684,499	8/1972	Hofer et al.....	75/211
		3,748,193	7/1973	Cech.....	148/101

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[*] Notice: The portion of the term of this patent subsequent to July 24, 1990, has been disclaimed.

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[21] Appl. No.: **491,608**

Related U.S. Application Data

[63] Continuation of Ser. No. 352,427, April 19, 1973, abandoned.

[52] U.S. Cl. **148/105; 148/31.57; 148/101; 148/103; 75/84; 75/152**

[51] Int. Cl.²..... **H01F 1/02**

[58] Field of Search 148/105, 103, 101, 100, 148/31.55, 31.57; 75/84, 84.5, 152, 211

[56] **References Cited**

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[57] **ABSTRACT**

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 halide, cobalt and calcium hydride is heated to effect reduction of the rare earth metal halide and to diffuse the resulting rare earth metal into the cobalt to form the intermetallic compound.

4 Claims, No Drawings

**RARE EARTH INTERMETALLIC COMPOUNDS
PRODUCED BY A REDUCTION-DIFFUSION
PROCESS**

This is a continuation of application Ser. No. 352,427, filed Apr. 19, 1973, now abandoned.

The present invention relates to rare earth intermetallic compounds and a reduction-diffusion process for preparing the compounds. These compounds are useful in the selective absorption of hydrogen and also in the fabrication of permanent magnets.

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_5 mischmetal, 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-rare earth intermetallic compound comprises heating the rare earth halide with calcium in a crucible above the melting point of the rare metal to reduce the halide and form an alloy of the rare earth metal and calcium. Cooling of the resulting product separates the rare earth metal from slag. The slag is removed and the bulk rare earth metal which is suitable only for melting stock 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.

In copending U.S. Patent application, Ser. No. 172,290 filed Aug. 16, 1971 in the name of Robert E. Cech now U.S. Pat. No. 3,748,193 and assigned to the assignee hereof, there is disclosed and claimed a process for preparing a magnetic material comprised of a particulate rare earth intermetallic compound. The process includes providing a particulate mixture of rare earth metal oxide, calcium hydride and a metal such as cobalt or iron, or alloys or mixtures thereof which can also include manganese, or alloys, or mixtures of either cobalt or iron with manganese; heating the particulate mixture in a non-reactive atmosphere to decompose the calcium hydride and thereby effect reduction of the rare earth metal constituent; and then heating the resulting mixture to diffuse the resulting rare earth metal into the aforementioned metal to form the rare earth intermetallic compound which is then recovered from the mixture.

In the present invention cobalt-rare earth intermetallic compounds as well as certain other metal-rare earth intermetallic compounds are prepared directly from the rare earth metal halide and the corresponding metal powder. This process eliminates the necessity of the separate steps of past processes of forming the rare earth bulk metal product as well as such steps as melting the rare earth metal with, for example, cobalt, cast-

ing 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 providing a halide of a rare earth metal except samarium, europium and ytterbium. A particulate mixture of the rare earth metal halide, calcium hydride and cobalt, is heated in a non-reactive atmosphere to decompose the calcium hydride and thereby effect reduction of the rare earth metal constituent. The resulting mixture is heated in a non-reactive atmosphere to diffuse the resulting rare earth metal into the cobalt to form the rare earth intermetallic compound or alloy. The rare earth intermetallic compound-containing mixture is then treated to recover the rare earth intermetallic compound or alloy.

In the present process, it is actually calcium resulting from the decomposition of the calcium hydride which acts to reduce the rare earth halide to form the rare earth metal. Hydrogen does not reduce rare earth halides to form rare earth metals to any significant amount. Calcium hydride is used because it is brittle and pulverizable and thus can form a thorough particulate mixture with the rare earth halide so that it can act on the halide effectively. In contrast to calcium hydride, calcium metal is ductile and cannot be formed into a powder to provide the necessary contact with the halide particles to reduce them satisfactorily. One particular advantage of the use of calcium hydride in the present process is that calcium does not alloy with the cobalt-rare earth alloy.

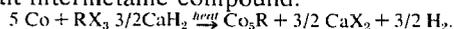
Another advantage of the present process is that the particle size of the cobalt-rare earth intermetallic compound or alloy produced is predetermined because it is nearly the same as the particle size of the cobalt particles initially used. Since cobalt powder is presently commercially available in a wide range of particle sizes and size distributions, the present process is useful to produce the 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. An additional advantage of the present process is that the particles of cobalt-rare earth intermetallic compound or alloy 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.

The halides of the rare earth metals useful in the present process are those of the rare earth metals which are the elements of the lanthanide series having atomic numbers of 57 to 71 but excluding samarium, europium and ytterbium. Specifically, the halides of the rare earth metals of the present invention are those of cerium, neodymium, praseodymium, promethium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, lutetium, and ytterbium.

lithium, lutetium, yttrium, lanthanum and mischmetal. 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. Mischmetal 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. Mixtures of rare earth metal halides can also be used. Samarium, europium and ytterbium are not useful in the present invention since they exist in a highly stable rare earth⁺⁺ state when combined with chlorine or other halogen and calcium or calcium hydride are unable to effect reduction of these partially reduced rare earths to the metallic state.

Considering the process of this invention in more detail, the following equation represents the stoichiometric reaction for forming Co_3R , where R is a rare earth metal except samarium, europium and ytterbium by the reduction of the rare earth from the halide, where X indicates the halide, to a constituent of the cobalt intermetallic compound:



Substantially stoichiometric amounts of the active constituents, cobalt, the rare earth halide 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 halide 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 halide 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 or alloy. The resulting product mass can then be placed in air or other oxygen and moisture-containing atmosphere to allow the precipitated calcium to oxidize or hydrolyze to disintegrate the mass and release the particles of the cobalt-rare earth intermetallic compound or alloy.

The rare earth halide can vary in particle size. It is available in commerce generally as a powder ranging from about 1 to about 10 microns or in precipitated form, which is a very fine particle size, i.e. of the order of 0.1 micron. The smaller the particle size, the faster the halide is reduced, and the resulting rare earth metal is thereby made available for diffusion into the cobalt in a shorter period of time.

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 in most instances 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 when the material is to be used as a permanent magnet 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. However, when the material is to be used for the selec-

tive absorption of hydrogen, it preferably ranges in size from about 10 to 50 microns since such a size is coarse enough to inhibit significant oxidation and also provide sufficient surface area for the significant absorption of hydrogen.

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 halide 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 halide are thoroughly mixed so that in carrying out the reaction, the calcium hydride, which is the reducing agent, can act on the halide 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 metal halide. 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 1,000°C. Substantially all the rare earth metal halide 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

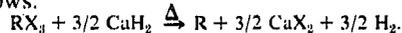
temperature of about 1,050° to 1,100°C for mischmetal to diffuse into cobalt of particle size from 1 to 5 microns. For cobalt powder having a particle size of 10-20 microns, about 2 hours in a substantial vacuum at a temperature of 1,050°-1,100°C is sufficient to accomplish the mischmetal diffusion. 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 calcium 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 percent 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 halide. In another method, where calcium bromide, chloride or iodide are present in the product, water or alcohol are added to the particulate product to dissolve out these calcium halides. The cobalt rare earth intermetallic compound particles can be dried in a conventional manner.

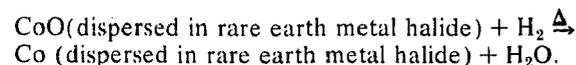
In the present process, if desired, the calcium hydride can be formed in situ by a number of methods. One method comprises admixing calcium metal pieces with the rare earth metal halide and cobalt and heating the mixture in the presence of hydrogen to form the calcium hydride and the mixture is then preferably re-ground to produce a thorough blend. In another method magnesium chips or powder are admixed with calcium oxide and heated in hydrogen to form calcium hydride and magnesium oxide which can 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 halide is initially admixed with the calcium to effect reduction of the rare earth metal constituent. Specifically, the rare earth halide powder, RX_3 , where X indicates the halide, is admixed with calcium hydride, and the mixture is then heated to effect reduction of the rare earth metal constituent. Specifically, the stoichiometric reaction for this embodiment is as follows:



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

In another embodiment of the present process, cobalt oxide instead of metallic cobalt, is initially mixed with the rare earth halide 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:



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

The present process is also useful in forming the entire range of cobalt-rare earth intermetallic compounds or alloys other than Co_3R , where R is the rare earth metal as defined herein, 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_3R , can be used in the present process along with proper amounts of the active constituents to produce Co_3R .

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 oxides (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 example where all heating was carried out in an electric hydrogen furnace, i.e. a furnace provided with hydrogen atmosphere.

EXAMPLE

Flakes of mischmetal chloride were vacuum dried for about 24 hours and then were ground to a powder. 59.5 grams of cobalt oxide having a particle size of about 1 micron were reduced in hydrogen at a temperature of 600°C for 8 hours to produce cobalt metal powder. This powder was mixed with 36.5 grams of the mischmetal chloride and 11.6 grams of 6 mesh calcium metal granules.

The resulting mixture was heated in hydrogen at a temperature of 850°C for about 15 minutes to form calcium hydride and then placed in the cold chamber of the furnace where it cooled to room temperature in hydrogen. The product was then pulverized and mixed by grinding under a nitrogen atmosphere.

The resulting mixture was heated in hydrogen at a temperature of 850°C for 2 hours. The temperature was then raised to 900°C, 950°C and 1,000°C where it was kept for ½ hour at each of these temperatures and

then raised to 1,050°C where it was maintained for 2 hours to diffuse the mischmetal into the cobalt.

The resulting reacted cake was cooled to room temperature and placed in a moist nitrogen atmosphere for 4 days where it broke down into a substantially flowable particulate material due to the hydration of excess metallic calcium. This material was ball milled for 1 hour to break up agglomerates. The resulting powder was repeatedly washed in water to remove the calcium chloride and calcium hydroxide therein, then washed with dilute acetic acid and then with alcohol after which it was dried under vacuum.

About 6 percent by weight of the resulting powder had a particle size of +200 mesh, about 11 percent by weight of the powder ranged in size from -200 to +325 mesh and about 69 percent by weight of the powder had a size of -325 mesh.

A portion of the dried product was subjected to X-ray diffraction analysis using the Debye-Scherrer technique. The X-ray powder pattern obtained indicated that it contained a major amount of single phase Co_5MM and a minor amount of $\text{Co}_{17}\text{MM}_2$ where MM is mischmetal.

81.1 percent of the powder was admixed with 19.9 percent of a particulate additive alloy composed of 60 percent by weight samarium and 40 percent by weight cobalt to form a substantially thorough mixture of 63 percent by weight cobalt with the remainder being samarium and mischmetal. A magnetic field of the mixture was compressed in an axial field of about 60,000 oersteds to align the particles along the easy axis. The green body was then sintered in an inert atmosphere of purified argon at a temperature of 1,105°C for 1 hour and then furnace-cooled in the same purified argon atmosphere. The sintered product had a density of 93 percent of theoretical.

The sintered product was magnetized along the easy axis at room temperature in a field of 60,000 oersteds and its magnetic properties were then determined. It was magnetic and had a saturation induction, B_s , of 9.77 kilogauss.

In copending U.S. Patent application Ser. No. 345,559, filed on Mar. 28, 1973, now abandoned in favor of Continuation Ser. No. 491,473 filed on July 24, 1974, in the name of Donald L. Martin and assigned to the assignee hereof, there is disclosed and claimed a process for preparing particles of nickel-lanthanum alloy having a composition within 15 percent by weight of the stoichiometric composition of Ni_5La intermetallic compound comprising providing a particulate mixture of lanthanum oxide, calcium hydride and nickel, heating the particulate mixture in a non-reactive atmosphere to decompose the calcium hydride and thereby effect reduction of the lanthanum constituent, and then heating the resulting mixture in a non-reactive atmosphere to diffuse the resulting lanthanum metal

into the nickel particles to form the alloy and recovering from the alloy-containing mixture the particles of the alloy.

In copending U.S. Patent application Ser. No. 345,560, filed on Mar. 28, 1973, now abandoned in favor of Continuation Ser. No. 497,527, now abandoned in the name of Donald L. Martin and assigned to the assignee hereof, there is disclosed and claimed a process for preparing particles of nickel-lanthanum alloy having a composition within 15 percent by weight of the stoichiometric composition of Ni_5La intermetallic compound comprising providing a particulate mixture of lanthanum halide, calcium hydride and nickel, heating the particulate mixture in a non-reactive atmosphere to decompose the calcium hydride and thereby effect reduction of the lanthanum constituent, and then heating the resulting mixture in a non-reactive atmosphere to diffuse the resulting lanthanum metal into the nickel particles to form the alloy and recovering from the alloy-containing mixture the particles of the alloy.

What is claimed as new and desired to be secured by Letters Patent of the United States is:

1. A process for preparing a magnetic material comprised of a particulate rare earth intermetallic compound comprising providing a halide of a rare earth metal except samarium, europium and ytterbium, admixing in at least substantially stoichiometric amounts particles of said rare earth metal halide, calcium hydride and a solid metal selected from the group consisting of cobalt, cobalt-manganese alloys, cobalt-iron-manganese alloys or cobalt-iron alloys, heating the resulting particulate mixture in an atmosphere which is inert to it at a temperature ranging from about 850°C to about 1,000°C decomposing said calcium hydride and effecting reduction of said rare earth metal halide to produce the rare earth metal, continuing heating the resulting mixture in an atmosphere which is inert to it at a temperature which diffuses the resulting rare earth metal into said solid metal group member to form the rare earth intermetallic compound, and recovering from the rare earth intermetallic compound-containing mixture said rare earth intermetallic compound.

2. A process according to claim 1 wherein calcium hydride is used in an amount in excess of stoichiometric and the resulting rare earth intermetallic compound-containing mixture is left in an oxidizing or moisture-containing atmosphere to allow the excess calcium precipitated therein to oxidize or hydrolyze causing said mixture to disintegrate.

3. A process according to claim 1 wherein said metal group member is cobalt and said rare earth halide is mischmetal chloride.

4. A process according to claim 1 wherein said calcium hydride is formed in situ.

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