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[54] **RECOVERY OF RARE-EARTH ALLOY PARTICLES FROM CALCIUM-CONTAINING PRODUCT USING AQUEOUS AMMONIUM CHLORIDE**

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[51] **Int. Cl.**[2] **H01F 1/02**

[58] **Field of Search** 148/105, 103, 101, 100, 148/31.57; 75/84, 152, 121

[56] **References Cited**

UNITED STATES PATENTS

2,123,617	7/1938	Vaughn	75/121
3,625,779	12/1971	Cech	148/101
3,748,193	7/1973	Cech	148/101

OTHER PUBLICATIONS

Latimer, W, et al; Reference Book of Inorganic Chemistry; New York, 1951 p. 458.

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[57] **ABSTRACT**

An aqueous solution of ammonium chloride is admixed with a material comprised of calcium hydroxide, calcium oxide and rare earth alloy particles. The ammonium chloride reacts with and dissolves the calcium hydroxide and oxide and has no significant effect on the rare earth alloy particles which have useful magnetic properties.

2 Claims, No Drawings

RECOVERY OF RARE-EARTH ALLOY PARTICLES FROM CALCIUM-CONTAINING PRODUCT USING AQUEOUS AMMONIUM CHLORIDE

The present invention relates to a rare earth alloy containing product produced by a reduction-diffusion process, and particularly to the recovery of rare earth alloy particles from such product without significantly deteriorating their potential magnetic properties.

U.S. Pat. No. 3,748,193, which is assigned to the assignee hereof and which by reference is made part of the disclosure of the present application, relates to a reduction-diffusion process for producing rare earth intermetallic compounds or alloys. Briefly stated, one embodiment of the disclosed process comprises providing a particulate mixture of a rare earth metal oxide, calcium hydride and a metal such as cobalt or iron, or alloys or mixtures thereof which can also include manganese; heating the particulate mixture in a non-reactive atmosphere to decompose the calcium hydride and thereby effect reduction of the rare earth metal oxide constituent, then heating the resulting mixture in a non-reactive atmosphere to diffuse the resulting rare earth metal into the aforementioned metal particles to form the desired rare earth intermetallic alloy particles which are then recovered from the product.

It is actually calcium resulting from the decomposition of the calcium hydride which acts to reduce the rare earth oxide to form the rare earth metal. If desired, the calcium hydride can be formed in situ by a number of methods. One particular advantage of the use of calcium hydride is that calcium does not alloy in any significant amount with the cobalt-rare earth or other magnetic rare earth alloys formed herein.

The oxides of the rare earth metal useful in the disclosed patented process are those of the rare earth metals which are the 15 elements of the lanthanide series having atomic numbers 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 mischmetal oxides (M_2O_3), mischmetal 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.

A number of rare earth intermetallic alloys can be formed merely by using the proper amounts of the active constituents. 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 alloy using samarium as an example:

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

U.S. Pat. No. 3,748,193 discloses that 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, and that 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.

When an excess amount of calcium hydride is used, a reaction product cake is produced wherein particles of rare earth intermetallic alloy, for example, cobalt-rare earth alloy, are substantially or completely surrounded by calcium and/or calcium oxide. Also, depending on the particular reaction conditions and atmospheres with which the product cake is contacted, calcium hydride and calcium nitride may also be present, usually in minor amounts, at or between the boundaries of the alloy particles.

This product can be hydrated by a number of techniques to react its calcium and calcium compound content to produce calcium oxide and calcium hydroxide from which the alloy particles are then separated.

A substantially self-regulting uniform hydration technique for disintegrating the cake or lumps thereof is disclosed in copending application Ser. No. 475,900 filed June 3, 1974 which is assigned to the assignee hereof and which, by reference, is made part of the disclosure of the present application. Specifically, the referred to copending application discloses the selection of a support screen having holes through which material of a desired size will pass and which is placed within a hydration zone. The reaction product cake is placed on the screen and a water vapor-carrying gas, wherein the gas cmponent is substantially inert, is passed through the zone to react with calcium and/or calcium compounds in the cake to produce calcium hydroxide. The resulting volume expansion disintegrates the cake between and along the boundaries of the particles. The disintegrated portions fall through the holes in the screen away from substantial contact with the incoming water vapor-carrying gas. The disintegrated product, i.e., the resulting hydrated powder, is comprised of calcium hydroxide, calcium oxide and particles of the rare earth alloy.

The present process uses an aqueous solution of ammonium chloride to recover the rare earth alloy particles from the hydrated reaction product cake, i.e., the material comprised of calcium hydroxide, calcium oxide and rare earth alloy particles. The aqueous solution of NH_4Cl is at least as effective as a dilute acid, such as acetic acid, in removing the calcium hydroxide and calcium oxide. Also, in contrast to acetic acid, the aqueous solution of NH_4Cl results in negligible dissolution of the rare earth alloy particles, for example Co_5Sm alloy particles. In addition, the aqueous NH_4Cl solution is less destructive towards materials such as the relatively labile, Sm-rich Co_7Sm_2 phase.

Briefly stated, the process of the present invention comprises providing a material comprised of calcium hydroxide, calcium oxide and rare earth alloy particles, said alloy particles having an average size less than 40 microns and consisting essentially of rare earth metal and a metal selected from the group consisting of cobalt, iron, manganese and alloys thereof, which comprises admixing said material with an aqueous solution of NH_4Cl, having from 2.1 to 3 moles of NH_4Cl dissolved therein for each mole of calcium oxide and calcium hydroxide present, said aqueous solution of NH_4Cl substantially dissolving said calcium oxide and hydroxide and having no significant effect on said rare earth alloy particles and recovering said alloy particles from the resulting mixture.

The material used in the process of the present invention, i.e., the hydrated reaction product cake material, is comprised of rare earth alloy particles which are surrounded by a significant extent by calcium hydroxide and calcium oxide. The total content of calcium hydroxide and calcium oxide generally ranges from 10 to 30% by weight of the rare earth alloy particles. The specific amount of calcium hydroxide or calcium oxide may vary and depends largely on the degree to which the material has been hydrated.

The process of the present invention is based on using an aqueous solution of ammonium chloride, NH_4Cl, to recover the rare earth alloy particles from the hydrated material. Since NH_4^+ is a weak acid, an aqueous NH_4Cl solution is weakly acidic. Specifically, when NH_4Cl is dissolved in water at room temperature it forms a potentially highly buffered solution having an initial pH of about 4.7. When an aqueous solution of NH_4Cl is admixed with the present material comprised of calcium hydroxidie, calcium oxide and rare earth alloy particles, the NH_4Cl preferentially reacts with the $Ca(OH)_2$ and CaO, which are sparingly soluble in water, to produce products which are highly soluble in water. This is illustrated by the following equations:

$$CaO + 2\ NH_4Cl + H_2O \rightarrow CaCl_2 + 2\ NH_4OH$$

$$Ca(OH)_2 + 2\ NH_4Cl \rightarrow CaCl_2 + 2\ NH_4OH.$$

To insure the substantial dissolution of CaO and CaOH in the present invention, at least 2.1 moles of NH_4Cl should be used for every mole of CaO and $Ca(OH)_2$ present. For best results, from 2.1 to 3.0 moles of NH_4Cl are used for every mole of $Ca(OH)_2$ and CaO present. As the dissolution of the calcium hydroxide and calcium oxide proceeds, the pH of the reaction solution shifts to higher values. An excess of NH_4Cl should be used to guarantee completion of the desired reaction.

In practice a saturated aqueous solution of NH_4Cl is used, i.e., about 30 grams of NH_4Cl per 100 ml H_2O at room temperature, to minimize the amount of water in contact with the rare earth alloy particles and thereby minimize the deterioration of magnetic properties of the rare earth alloy particles by water. One particular advantage of the present process is that as NH_4Cl dissolves in water at room temperature it lowers the temperature of the water. Since the reaction of NH_4Cl with the present calcium containing material is exothermic, the use of a cool solution without employing external coolants is advantageous particularly since a highly exothermic reaction will oxidize and deteriorate the magnetic properties of the rare earth alloy particles.

In carrying out the present process, the aqueous NH_4Cl solution is admixed with the hydrated material and the resulting mixture or slurry should be stirred to hasten the approach to completion. Equilibrium is determinable empirically by standard techniques, for example, titrating samples of the reaction solution or using a pH meter. In the present process where 2.1 to 3 moles of NH_4Cl are used for each mole of CaO and $Ca(OH)_2$ present, from 5 to 30 minutes is sufficient time for the dissolution.

The rare earth alloy particles are recovered from the reaction solution, i.e., leach solution, by a number of conventional techniques. For example, the reaction solution can be decanted and the rare earth alloy particles washed with water, then alcohol and then dried in an atmosphere in which they are inert such as argon or a vacuum to prevent any significant oxidation and loss of potential magnetic properties. The yield of rare earth alloy particles recovered is greater than 90% of theoretical and usually does not contain more than 0.1% by weight calcium in any form.

In one embodiment of the present process the hydrated material comprised of CaO, $Ca(OH)_2$ and rare earth alloy particles in initially admixed with water causing some of the CaO to form $Ca(OH)_2$. When the water is decanted, flocculent $Ca(OH)_2$ precipitate is decanted with it, causing about 90% of the calcium content of the material to be removed before contact with the aqueous solution of NH_4Cl.

The present invention is further illustrated by the following example.

EXAMPLE

A control experiment was carried out on a lot of Co_5Sm (35 weight % Sm) nominal) alloy powder prepared by the reduction-diffusion process disclosed in U.S. Pat. No. , 3,748,193. The reacted mixture was hydrated to convert the relatively hard cake to a powder, as well as to convert all unreacted Ca metal to CaO and $Ca(OH)_2$. Knowing the initial amount of calcium hydride used in the reductiondiffusion process, it was calculated that the total amount of CaO and $Ca(OH)_2$ present was approximately 25% by weight of the Co_5Sm alloy powder. The entire lot was then homogenized and divided into two equal mass aliquots. The first aliquot, A, was processed by magnetic separation to remove the free lime followed by an acetic acid leach to remove the remaining lime content, i.e., CaO and $Ca(OH)_2$. The acetic acid leach was about a 5% by volume aqueous acetic acid solution and was stirred with the alloy powder for 15 minutes. The solution was then decanted and the Co_5Sm powder was washed with H_2O, rinsed with alcohol, and dried in a vacuum.

The second powder aliquot, B, was placed in a vessel containing 20 liters of cold, deionized H_2O in which was dissolved 1.5 times the stoichiometric amount of NH_4Cl required to convert the lime content to $CaCl_2$ and NH_4OH. The 50% excess of NH_4Cl was used to insure rapid reaction. The Co_5Sm powder was stirred with the NH_4Cl solution for 15 minutes. The solution was then decanted off and the powder washed eight times with deionized H_2O. The Co_5Sm powder was then rinsed with alcohol and vacuum-dried.

Four samples from each processed Co_4Sm powder aliquot were submitted for chemical analysis. The analytic result, along with the process parameters, are given in the following table.

	Aliquot A Acetic Acid Leach	Aliquot B Ammonium Chloride Leach
Initial Aliquot Mass (lbs.)	21.25	21.25
Volume Acetic Acid (ML)	800	—
Mass Ammonium Chloride (lbs.)	—	15.2
Final Aliquot Mass (lbs.)	15.95	17.34
Yield* (%)	89.4	97.1
Chemical Analysis**		
Weight % Ca	0.093	0.090
Co	64.58	64.23
Sm	34.59	34.85
Fe	0.027	0.025
Ni	0.067	0.070
Al	0.047	0.047

-Continued

	Aliquot A Acetic Acid Leach	Aliquot B Ammonium Chloride Leach
X-ray Diffraction Analysis	Co_5Sm + traces of Co_7Sm_2.	Co_5Sm + traces of Co_7Sm_2 — more than in Aliquot A

*The anticipated yield per aliquot based on initial mass or reactants was 17.85 lbs.

**The values are averages of the four values obtained for the samples submitted.

The above Table illustrates that NH_4Cl is at least as effective as acetic acid in removing CaO and $Ca(OH)_2$. The Table also shows that the NH_4Cl solution results in negligible dissolution of the Co_5Sm powder in contrast to acetic acid. In addition, X-ray Diffraction Analyses indicated that NH_4Cl is less destructive toward the relatively labile, Sm rich Co_7Sm_2 phase than acetic acid.

What is claimed is:

1. A process for recovering rare earth alloy particles having useful magnetic properties from a material comprised of calcium hyroxide, calcium oxide and rare earth alloy particles, said calcium hydroxide and calcium oxide being present in an amount ranging from about 10% to 30% by weight of said rare earth alloy particles, said rare earth alloy particles having an average size less than 40 microns and consisting essentially of rare earth metal and a metal selected from the group consisting of cobalt, iron, manganese and alloys thereof which comprises admixing said material with an aqueous solution of NH_4Cl having a temperature below room temperature and having from 2.1 to 3 moles of NH_4Cl dissolved therein for each mole of calcium oxide and calcium hydroxide present, said aqueous solution of NH_4Cl reacting with and dissolving said calcium oxide and calcium hydroxide and having no significant effect on said rare earth alloy particles, said reaction having no significant deteriorating effect on the magnetic properties of said rare earth alloy particles, recovering said alloy particles from the resulting reaction solution, and drying said particles in an atmosphere in which they are inert.

2. A process according to claim **1** wherein said material is initially admixed with water and a significant amount of said calcium oxide and calcium hydroxide is decanted with said water.

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