

[54] **PROCESS FOR ENHANCING MAGNETIC
PROPERTIES OF METAL POWDER BY
HEAT TREATING WITH SALT**

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[57]

ABSTRACT

A process for enhancing the magnetic properties of small particulate ferromagnetic powders, e.g. particles below the critical diameter for which an untreated particle's domainboundary energy equals its magnetostatic energy, the process comprising heat treating said particles. In the more favorable embodiments of the invention, the particles are heated in intimate association with a particulate refractory material which serves as a shield for effectively preventing excessive sintering of the metal particles.

7 Claims, No Drawings

PROCESS FOR ENHANCING MAGNETIC PROPERTIES OF METAL POWDER BY HEAT TREATING WITH SALT

BACKGROUND OF THE INVENTION

This invention relates to a process for making magnetic particles formed of exceptionally small metal particles, and to the particles formed thereby.

In recent years there has been a great deal of activity in making small metallic particles for use in various fields of technology. For example, metal powders are utilized in catalytic-type processes wherein they may be carried on an inert carrier or may be used directly. Metal powders also find some utility in pyrotechnic formulations and in manufacture of special-purpose mixtures such as, for example, might be used in manufacture of magnets. Metal powders also find use in manufacture of magnetic tapes such as those used in information retrieval systems.

Very small metallic particles are particularly useful in a number of these applications because of their high surface area or some other such inherent property. It is often convenient that such very small metallic particles be magnetic. Magnetic characteristics not only make them useful for many special applications, but also make them more easily recoverable and easier to manipulate. However, it has remained a problem to produce metallic particles of high magnetic character when the particles are very small, e.g. below the so-called "critical diameter" of a given metal.

As disclosed by Thomas O. Paine at pages 149-150 of *Magnetic Properties of Metals and Alloys* published by American Society for Metals, Cleveland, O. (1959), the critical diameter is that for which a particle's domain-boundary energy equals its magnetostatic energy.

Clearly, then, the more ideally-arranged magnetic particles will have a higher magnetostatic energy than less ideally-arranged magnetic particles of the same size. This effect has been used by investigators such as Miller and Opegaard who, in work described in U. S. Pat. No. 3,206,338, caused very small particles to be produced in a magnetic field, thereby enhancing the arrangement of the atoms within each particle to provide a relatively ideal magnet; and, consequently obtaining greater magnetostatic energy for each particle than would have been achieved without use of a magnet. The resulting particles exhibit magnetic behavior at unusually small particle sizes, i.e. particle sizes in the order of 0.01 micron (100 Angstroms) in cross-sectional direction and 0.05 microns (500 Angstroms) in length.

This utilization of a magnetic field, although practically employed on a laboratory basis, does present practical problems when it is scaled up for production of commercial quantities of metal powders. Moreover, the products produced thereby are still not at their optimum order. An alternative, less cumbersome, method of achieving very small, yet magnetic, particles is desirable.

SUMMARY OF THE INVENTION

Therefore, it is an object of the invention to provide a novel process for making very small magnetic particles.

Another object is to provide means to enhance the magnetic properties by a thermal treatment while minimizing any sintering of said particles.

Other objects of the invention will be obvious to those skilled in the art on reading this application.

The above objects have been accomplished by heat treating small ferromagnetic metallic powders at temperatures high enough to permit a crystalline or atomic rearrangement within the metal particle.

The most advantageous means for producing said powders is believed to be by reduction of a soluble metallic salt to the metal by a strong reducing agent, e.g. a metal borohydride like sodium borohydride. However, formation of metal particles by decomposition of metal carbonyls or by other precipitation reactions, may also be used to provide particles for use in the invention.

The term ferromagnetic as used herein is meant to cover not only alpha iron, cobalt, nickel, gadolinium and dysprosium, but is also meant to cover materials such as the Heusler-type alloys which are ferromagnetic, albeit the individual elemental components thereof are not. These latter compositions include manganese alloys with copper and aluminum or indium, with arsenic and with antimony. The manganese atom therein is generally considered to contribute the ferromagnetic activity in the alloy environment.

Heat treatment temperatures in the range of from 250°C to 650°C have proven effective with cobalt, iron, and mixtures thereof. Those skilled in the metallurgical arts will understand that the heat cycle will have various equivalents when higher temperatures are used for shorter times or when lower temperatures are used for longer times.

In a particularly advantageous embodiment of the invention, the thermal treatment is carried out while maintaining the metal particles in intimate contact with a refractory substance, say a high-melting salt like sodium chloride. The presence of such a refractory material has been found to substantially inhibit excessive sintering of the metal particles during heat treatment. The presence of the refractory material is particularly important at higher temperatures at which the particles tend to undergo a favorable realignment more readily. At such temperatures, the tendency for particulate sintering is particularly high.

The refractory substance should usually have some physical or chemical property which makes it readily separable from the magnetic particles. Mere differential magnetism is not usually a convenient means although it can be utilized for magnetic separation. Differential specific gravity can be exploited in a centrifugal separation process. It is usually more advantageous to use a chemical parameter such as water solubility to effect the separation of the refractory material from the metal. Thus water-soluble salts such as sodium chloride, etc., are most advantageously used.

ILLUSTRATIVE EMBODIMENT OF THE INVENTION

In order to point out more fully the nature of the present invention, the specific embodiments of the present process and products produced thereby are set forth below:

Working Example 1

A quantity of 71.4 grams of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 300 milliliters water. In a second vessel, 11.4 grams of sodium borohydride were dissolved in 300 milliliters of water.

The borohydride solution was charged into the cobalt salt solution and agitated with a magnetic stirrer. This resulted in the reduction of the cobalt to a particulate metal form.

The particulate metal was removed from the liquid medium with a strong magnet and washed ten times with 800 milliliters water and three times with 300 milliliters acetone, before being air-dried at 70°F for 1 hour and then vacuum dried for 4 hours at 70°F.

The dried cobalt powder was determined to have the following magnetic properties:

Saturation Magnetic Moment = 22 e m u/gram
Coercivity = 85 oersteds
Squareness = 0.35

The magnetic measurements set forth above and elsewhere in this specification were made on a vibrating string magnetometer. The samples were air-stable because they had been exposed to air before measurement and therefor had an oxide protective layer thereon. Generally, two hysteresis loops were traced for each sample; one at about 1 kilooersted peak-field and one at about 8 kilo-oersteds. This method is quantitative and requires only a small sample, e.g. several milligrams of the magnetic powder being measured.

Squareness is defined as the remanent magnetization divided by the saturation magnetic moment. Thus, remanence can be calculated by simply multiplying squareness by saturation magnetization.

A sample of 500 milligrams of the resulting particles were heat treated at 300°C under a hydrogen atmosphere for 30 minutes, cooled to room temperature while still under the hydrogen atmosphere, and purged with argon gas. Thereupon the magnetic properties were measured to be as follows:

Saturation Magnetic Moment = 48 e m u/gram
Coercivity = 356 oersteds
Squareness = 0.41

Working Example 2

A quantity of five grams of the cobalt powder, taken from the product of Working Example 1 before the heat treatment thereof, was mixed with 80 grams of very fine sodium chloride powder. This salt powder had all passed through a 425 mesh screen.

The particulate mixture was comminuted in a quart-capacity "ball-mill" jar with ceramic balls for 48 hours. Thereupon, eight grams of the powdery mixture was subjected to the same heat treatment as the material discussed in Example 1, i.e. 300°C for 30 minutes.

After the heat treatment the powder mix was washed four times with 100 milliliters of water and three times with 100 milliliters of tetrahydrofuran. The material was air dried, vacuum dried and its electromagnetic properties were measured to be as follows:

Saturation Magnetic Moment = 67 e m u/gram
Coercivity = 560 oersteds
Squareness = 0.38

The presence of the particulate sodium chloride during the heat-treating step resulted in about a 38 per cent increase in the saturation magnetic movement value and nearly a sixty per cent increase in the coercive force value over those values obtained when the salt was not present during the heat treatment, i.e. in the heat treatment of Example 1.

Working Example 3 — Effect of Increasing Temperature

In addition to the heat treatment at 300°C, described in each of Examples 1 and 2, the materials from each Example were heat-treated for thirty minutes at a series of higher temperatures with the following results:

Saturation Magnetic Moment

Temperature	Example 1 No Salt	Example 2 Salt Present
300°C	48	67
350°C	45	71
400°C	65	58
450°C	83	99
550°C	102	—
650°C	82	61

From the above results, it seems clear that further increases in temperature will not enable obtaining higher saturation magnetic moment values during a cobalt powder treatment period as long as 30 minutes.

Coercive Force

Temperature	Example 1 No Salt	Example 2 Salt Present
300°C	356	560
350°C	438	600
400°C	468	550
450°C	69	525
550°C	62	526
650°C	69	414

The optimum coercivity appears to be reached, during a 30-minute treatment of cobalt at a temperature below 450°C.

Squareness

Temperature	Example 1 No Salt	Example 2 Salt Present
300°C	0.41	0.38
350°C	0.42	0.35
400°C	0.38	0.35
450°C	0.18	0.33
550°C	0.14	0.33
650°C	0.08	0.28

What is apparent from all of these measurements is that heat-treatment in the presence of an inert refractory powder like sodium chloride allows the achievement of optimum magnetic properties at lower temperatures and that those properties achieved at the lower temperatures are (1) generally more favorable than could be achieved at any temperature for the salt-free powders and (2) more resistant to thermal decay than the properties of the salt-free powders.

Working Example 4

A quantity of 71.4 grams of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ was dissolved in 300 milliliters of water with 320 grams of sodium chloride which had passed a 425-mesh screen. This first solution was prepared in a Waring Blender.

A second solution, containing 11.4 grams of sodium borohydride in 100 milliliters of water, was prepared in a separatory funnel and then added dropwise to the Waring Blender at the slowest agitation speed. The addition was slow enough to keep the exothermic reaction between the two solutions from increasing the temperature of the reaction medium much above 35°C. Cobalt precipitated.

The precipitate, which included a large part of the original salt, was filtered, washed with 400 milliliters of acetone twice, redispersed in 400 milliliters of acetone, and air dried.

Forty grams of the dried material was enclosed in a glass container and heated to 350°C in a hydrogen atmosphere, maintained at 350°C for an hour, cooled while still under hydrogen, purged for 2 minutes with

argon at room temperature and washed four times with 800 milliliters of water and two times with 300 milliliters of tetrahydrofuran. A magnet, rather than a filter paper was used to effect separation of the cobalt particles from the wash liquids. The material was dried in air and vacuum dried.

The magnetic properties of the resulting material:

Saturation Magnetic Moment	91 e m u/gram
Coercivity	500 oersteds
Squareness	0.32

Working Example 5

Seventy-five milliliters of a 0.7 molar cobalt chloride and 0.3 molar FeCl_2 solution is charged into a small stainless steel mixer which is maintained in a strong magnetic field of about 1,500 oersteds. A quantity of 75 milliliters of a one molar, aqueous, sodium borohydride solution is slowly added to the solution of metal chlorides. The resultant reaction results in the precipitation of metallic particles which were washed several times with water, washed with tetrahydrofuran, separated from the liquid with a magnet after each wash, and air dried.

The magnetic properties of the resulting cobalt-iron mixture were measured to be as follows:

Saturation Magnetic Moment	40 e m u/gram
Coercivity	312 oersteds
Squareness	0.42

Heat treatment data will be given under Example 8.

Working Example 6

When the Example 5 was substantially repeated, but with 75 milliliters of a chloride solution 0.9 molar in cobalt chloride and 0.1 molar in FeCl_2 , the following magnetic properties were measured on the resulting product:

Saturation Magnetic Moment	33
Coercivity	88
Squareness	0.35

Heat treatment data will be given under Example 8.

Working Example 7

The powder product described in Example 5 is mixed with 16 times its weight of sodium chloride powder which had passed a 425 mesh screen. Eighty-five grams of the resulting mixture was dispersed in 300 milliliters of ethyl alcohol and ball milled for 24 hours using stone balls and a 1-quart capacity ceramic ball mill, then recovered and dried.

Heat treatment data will be given under Example 8.

Working Example 8

This example describes the heat treatment of the powders which were produced by the procedure described in Examples 5, 6 and 7.

Small samples of each of these materials were heat treated at various temperatures under an argon atmosphere. Each sample held at the treatment temperature for 80 minutes under an hydrogen atmosphere after being brought up to temperature under an argon atmosphere. Then the samples were cooled under hydrogen, and purged with argon. Each cooled sample was washed four times with water, washed four times with tetrahydrofuran, air dried and dried further under a vacuum.

In the following table the values of magnetic proper-

ties of the non-heated materials are placed in parentheses.

Treatment Temperature of 250°C

Product Source	Saturation Magnetic Moment	Coercivity	Squareness
Example 5	48 (40)	125 (312)	0.43 (0.42)
Example 6	58 (33)	200 (88)	0.44 (0.35)
Example 7	28	457	0.42

Treatment Temperature of 350°C

Product Source	Saturation Magnetic Moment	Coercivity	Squareness
Example 5	81 (40)	850 (312)	0.41 (0.42)
Example 6	7.4 (33)	250 (88)	0.41 (0.35)
Example 7	76	712	0.37

It is clear, therefore, that the process of the invention provides a means to improve the magnetic properties of particles produced by reduction of dissolved metal salts within a strong magnetic field.

It is of course to be understood that the foregoing examples are intended to be illustrative and that numerous changes can be made in the reactant proportions, and conditions set forth therein without departing from the spirit of the invention as defined in the appended claims.

What is claimed is:

1. In a process for making a magnetic metallic powder of the type comprising a major portion of cobalt metal wherein said process comprises the step of forming metal particles by reacting a reducing agent with a metallic salt in solution and a subsequent thermal treatment of dried metallic powder formed of said particles, the improvement comprising the steps of

A. intimately mixing a quantity of inorganic refractory salt powder material with said dried metal particles, said quantity being an amount effective to separate said metal particles from one another to markedly reduce the physical interaction of said metal particles during heating then

B. heat treating the resulting mixture at a temperature above 250° C. to enhance the magnetic properties thereof, and then

C. separating said metal particles from said refractory powder thereby providing a mass of magnetic metallic particles of enhanced magnetic properties.

2. A process as defined in claim 1 wherein said salt dust is water-soluble salt.

3. A process as defined in claim 1 wherein said heating is carried out for less than one hour at a temperature of about 450°C or below.

4. A process as defined in claim 1 wherein said heat treating is carried out at a temperature of about 350°C or below.

5. A process as defined in claim 1 wherein said heating is carried out until the coercive force exceeds 500 oersteds.

6. A process as defined in claim 1 wherein said heating is carried out until the coercive force exceeds 500 oersteds.

7. A fine magnetic powder of cobalt and formed according to the process defined by claim 1.

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