METHOD OF MANUFACTURING FE NANOPOWdERS BY CHEMICAL VAPOR CONDENSATION

Byung Kee Kim, Busan-shi (KR);
Dong Won Lee, Changwon-shi (KR);
Chul Jin Choi, Changwon-shi (KR)

Disclosed is a method of synthesizing Fe powders having sizes of tens of nm by vaporizing an iron atom-containing liquid material with a low melting point at high temperatures, and then condensing iron atoms in decomposed Fe and CO gas by chemical vapor condensation. According to the current invention, the synthesizing method includes vaporizing iron pentacarbonyl (Fe(CO)5) or iron acetate ((CH3CO2)2Fe) precursor to gas by use of a ceramic bubbler of a chemical vapor condensation device, decomposing the vaporized gas to Fe in a reactor of the device while being introduced with Ar gas, and condensing the decomposed Fe in a chamber of the device, thereby obtaining the Fe powders having sizes of tens of nm.
Fig. 3

- α-Fe
- γ-Fe
- Fe₃O₄

1000°C
800°C
600°C
400°C
METHOD OF MANUFACTURING Fe NANOPOWDERS BY CHEMICAL VAPOR CONDENSATION

RELATED APPLICATIONS

This application claims priority under 35 U.S.C. §119(a) to Korean Patent Application No. 10-2003-0077589, filed on Nov. 4, 2003 by Byung Kee Kim et al., entitled “METHOD OF MANUFACTURING Fe NANOPOWDERS BY CHEMICAL VAPOR CONDENSATION” the contents of which are hereby incorporated by reference in their entirety.

FIELD OF THE INVENTION

The present invention relates to a manufacturing method of iron nanoparticles, and more specifically, to a method of manufacturing nano-sized iron powders by means of chemical vapor condensation.

DESCRIPTION OF THE RELATED ART

Fine powders having magnetic properties, that is, fine magnetic powders, have various applications, for example, contrast media for magnetic resonators, recording media for magnetic tapes, magnetic fluid materials, etc. The magnetic powders presently commercially available, are exemplified by oxide-based powders, such as Fe₂O₃, Fe₃O₄, Fe-ferrite and Co-ferrite.

Conventionally, the magnetic powders have been mainly manufactured by a liquid reaction process, such as metal hydroxide reduction or metal salt reduction. In particular, the contrast medium having high quality and the magnetic fluid for scaling materials are possible to be manufactured by use of only material powders exhibiting superparamagnetic properties, which are fined to have a particle size not larger than a single magnetic domain. Accordingly, there required methods of synthesizing finer magnetic metal powders having further decreased particle sizes while improving magnetic properties thereof.

SUMMARY OF THE INVENTION

Accordingly, an object of the present invention is to alleviate the problems encountered in the related art and to provide a method of synthesizing metal iron powders having sizes of tens of nm, by vaporizing an iron atom-containing liquid material having a low melting point at high temperatures and then condensing iron atoms in decomposed Fe and CO gas by chemical vapor condensation.

To achieve the above object, the present invention provides a method of manufacturing Fe nanoparticles by chemical vapor condensation, including: vaporizing a Fe-containing liquid precursor to gas, to obtain a vaporized gas; decomposing the vaporized gas to Fe while being introduced with an inert gas, to obtain decomposed Fe; and condensing the decomposed Fe, to obtain Fe nanoparticles.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects, features and other advantages of the present invention will be more clearly understood from the following detailed description taken in conjunction with the accompanying drawings, in which:

FIG. 1 is a schematic view of a chemical vapor condensation device used in the present invention;
FIG. 2 is electron micrographs of Fe nanopowders manufactured at different reaction temperatures;
FIG. 3 is an X-ray diffraction spectrum for the Fe nanopowders of FIG. 2; and
FIG. 4 is enlarged electron micrographs of parts of the Fe nanopowders, in the Fe nanopowders of FIG. 2.

DETAILED DESCRIPTION OF THE INVENTION

Hereinafter, a detailed description will be given of the present invention, with reference to the appended drawings.

Useful in the present invention, a pure iron material has a magnetization value two or three times higher than that of oxide materials, and also, has low anisotropic properties, thus having a lower coercive force. Further, as a particle size of iron decreases, the magnetization value is constantly reduced while the coercive force is increased, whereby iron is possible to be used as a magnetic recording medium. Moreover, iron having a very small particle size comes to be a superparamagnetic material, and hence, is usable as a magnetic fluid.

To manufacture iron nanoparticles of the present invention, there is required a chemical vapor condensation device, which is schematically shown in FIG. 1. As apparent from FIG. 1, the device (1) includes a ceramic bubbler (3), a reactor (6), and a chamber (7).

A liquid precursor containing Fe is vaporized to gas by means of the ceramic bubbler (3). That is, the liquid precursor in a storage bath (2) is fed through a feeding pipe (5) and a feeder (4), and then is vaporized while passing through the ceramic bubbler (3) that is maintained at predetermined temperatures.

Suitable for use in the present invention, the Fe-containing liquid precursor is exemplified by iron pentacarbonyl (Fe(CO)₅), or iron acetate ((CH₃COO)₂Fe), in which iron pentacarbonyl having a vaporization point of about 103°C is easily vaporized at 150-220°C.

However, the gas vaporized by use of the ceramic bubbler (3) is not decomposed to Fe and CO gas in the above temperature ranges. Therefore, while the vaporized gas is introduced with an inert gas, it passes through the reactor (6) which is maintained at high temperatures, whereby Fe is decomposed from the vaporized gas. In the present invention, the reactor (6) is in the temperature range of 400 to 1000°C, and preferably, 400 to 800°C. If the temperature of the reactor (6) is higher than 1000°C, large quantities of γ-Fe phase are obtained, together with α-Fe. In such cases, the γ-Fe phase as a non-magnetic material negatively affects requirement properties of synthetic powders, which is unfavorable.

The decomposed Fe gas transferred to the reactor (6) along with the inert gas is condensed to the size of tens of nm therein, and is formed to be crystalline Fe powders, which are then sprayed into the chamber (7). In the chamber (7), the crystalline Fe gas is floated for several hours and then is attached to an inner wall or a bottom surface of the
chamber (7). Even after the precursor solution is completely fed, the floating of the Fe powders is continued for several hours in the chamber (7). The inert gas is continuously introduced into the chamber (7) until all the synthesized Fe powders are stably settled down, whereby the inside of the chamber (7) is maintained in a non-oxidative protection atmosphere and the CO gas remaining in a very small amount in the chamber (7) is discharged out of the chamber (7).

[0019] On the other hand, when the chamber (7) is opened as soon as the synthesized Fe powders are collected therein, it may be exploded. Hence, before the chamber (7) is opened, a small amount of oxygen is fed into the chamber (7) through an inlet (8) thereof, and thus, the iron nanopowders are coated with an oxide layer. Like this, it is preferred that the iron nanopowders are subjected to passivation treatment to be stably handled under atmosphere.

[0020] A better understanding of the present invention may be obtained through the following examples which are set forth to illustrate, but are not to be construed as the limit of the present invention.

**EXAMPLE 1**

[0021] Iron pentacarbonyl as a liquid precursor was fed into a chemical vapor condensation device of FIG. 1, thus manufacturing Fe powders. As such, a ceramic bubbler (3) of the above device was maintained in a range of 150-200°C, and the liquid precursor was fed at 0.30 g/min. Then, while Ar gas was introduced at 2000 cc/min into the ceramic bubbler (3), the vaporized gas passed through a reactor (6) and then was sprayed into a chamber (7). The reactor was formed with a virtually pure alumina tube having an inner diameter of 5 mm and a length of 300 mm, and was in the temperature range of 400 to 1000°C.

[0022] In addition, before the chamber (7) was opened, air was introduced at 2000 cc/min into the chamber (7), whereby an oxide coating layer was formed on the respective Fe powders.

[0023] The manufactured Fe powders were observed by means of an electron microscope. The results are depicted in FIG. 2. As apparent from electron micrographs of FIG. 2, the Fe powders have an average particle size of 8, 17 and 68 nm when the synthesizing temperatures are 400°C, 600°C and 800°C, respectively, as is apparent from FIG. 2, the Fe powders synthesized at 400°C, 600°C and 800°C, respectively, have an amorphous type peak of Fe3O4. Although the Fe powders synthesized at 800°C, 1000°C and 1200°C, respectively, have such an oxide, the pressure of the Fe powders synthesized at 1000°C and 1200°C are very small compared to the increased particle size of iron. In cases of the Fe powders synthesized at 1000°C and 1200°C, large quantities of γ-Fe, which have a bad effect on the properties of the synthesized powders, are present, together with α-Fe.

[0024] FIG. 3 shows analytic results of X-ray diffraction patterns of Fe powders according to reaction temperatures. As shown in FIG. 3, the Fe powders synthesized at 400°C and 600°C C., respectively, have an amorphous type peak of Fe3O4. Although the Fe powders synthesized at 800°C and 1000°C, respectively, have such an oxide, they have no X-ray diffraction peak. This is because the above oxide has a very small volume compared to the increased particle size of iron. In cases of the Fe powders synthesized at 1000°C and 1200°C, large quantities of γ-Fe, which have a bad effect on the properties of the synthesized powders, are present, together with α-Fe.

**EXAMPLE 2**

[0026] Fe powders were synthesized in the same manner as in Example 1, with the exception that the liquid precursor was fed at 0.15 g/min and reacted at 600°C. (inventive example 3). The Fe powders had an average particle size of 16 nm. From this, it can be found that a slow feeding rate of the precursor solution does not greatly affect the fineness of Fe powders.

**EXAMPLE 3**

[0027] The Fe nanopowders manufactured in Examples 1 and 2 were measured for magnetic properties, such as coercive force and maximum magnetization value. The results are summarized in Table 1, below, along with process conditions of Fe powders.

<table>
<thead>
<tr>
<th>Feeding Rate (g/min)</th>
<th>Reactor Temp. (°C)</th>
<th>Fe-Core (nm)</th>
<th>Oxygen Conc. (wt %)</th>
<th>Fe3O4 Shell (nm)</th>
<th>Coercive Force (Oe)</th>
<th>Max. Magnet. Value (emu/g)</th>
<th>Note</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.30</td>
<td>400</td>
<td>8</td>
<td>14.2</td>
<td>2.5</td>
<td>745</td>
<td>125</td>
<td>Inv. Ex. 1</td>
</tr>
<tr>
<td>0.30</td>
<td>600</td>
<td>17</td>
<td>13.6</td>
<td>3.4</td>
<td>998</td>
<td>147</td>
<td>Inv. Ex. 2</td>
</tr>
<tr>
<td>0.15</td>
<td>600</td>
<td>16</td>
<td>13.5</td>
<td>3.4</td>
<td>1021</td>
<td>145</td>
<td>Inv. Ex. 3</td>
</tr>
<tr>
<td>0.30</td>
<td>800</td>
<td>68</td>
<td>3.8</td>
<td>3.6</td>
<td>103</td>
<td>205</td>
<td>Inv. Ex. 4</td>
</tr>
<tr>
<td>0.30</td>
<td>1000</td>
<td>96</td>
<td>2.6</td>
<td>3.8</td>
<td>95</td>
<td>76</td>
<td>C. Ex.</td>
</tr>
</tbody>
</table>

Since the Fe powders manufactured at 1000°C have a considerable amount of a nonmagnetic material, γ-Fe, magnetic properties thereof becomes insignificant. However, as for the Fe powders synthesized at temperatures not higher than 800°C, the coercive force increases up to 1021 Oe until the average particle size decreases to 16 nm, and then, is reduced again at the particle size of 10 nm or less. It is believed that superparamagnetic properties appear on much smaller to particles among the Fe powders having an
average size of 8 nm. In common, the finer the particles, the higher the spin non-arrangement effects based on increase of surface areas. Hence, the maximum magnetization value may decrease even to about 50% or less of a maximum value of a bulk material. For example, a theoretical maximum magnetization value of bulk pure iron amounts to 225 emu/g, while the maximum magnetization value of iron of the present invention decreases from about 200 emu/g to about 120 emu/g by particle fineness.

[0029] As described hereinbefore, the present invention provides a method of manufacturing Fe nanopowders by chemical vapor condensation, characterized in that sizes, phases and magnetic properties of the synthesized Fe nanopowders can be controlled according to reaction temperatures. The Fe nanopowders of the present invention is applicable as a magnetic recording medium. Further, through process improvement, such as decrease of the reaction temperatures, the Fe powders can be further fined, whereby they can be used as a magnetic fluid.

[0030] Although the preferred embodiments of the present invention have been disclosed for illustrative purposes, those skilled in the art will appreciate that various modifications, additions and substitutions are possible, without departing from the scope and spirit of the invention as disclosed in the accompanying claims.

What is claimed is:

1. A method of manufacturing Fe nanopowders by chemical vapor condensation, comprising:
   vaporizing a Fe-containing liquid precursor to gas, to obtain a vaporized gas;
   decomposing the vaporized gas to Fe while being introduced with an inert gas, to obtain decomposed Fe; and
   condensing the decomposed Fe, to obtain Fe nanopowders.

2. The method as defined in claim 1, wherein the liquid precursor comprises iron pentacarbonyl (Fe(CO)5), or iron acetate ((CH3COO)2Fe).

3. The method as defined in claim 1, wherein the decomposing of the vaporized gas is performed at 400 to 800°C.

4. The method as defined in claim 1, wherein the condensing of the decomposed Fe further comprises feeding oxygen to coat each surface of the Fe nanopowders with an oxide layer.

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