Synthesis and characterization of NiFe_2O_4 nanopowders via spray pyrolysis

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NiFe_2O_4 powders with large-sized, hollow, and thin wall structures were directly prepared by spray pyrolysis from a spray solution containing citric acid. These as-prepared powders converted into nanosized NiFe_2O_4 powders after post-treatment at high temperatures between 600 and 1000°C. Phase-pure NiFe_2O_4 powders were obtained at post-treatment temperatures between 700 and 1000°C. When the post-treatment temperatures were increased from 700 to 1000°C, the BET surface areas of the NiFe_2O_4 powders decreased from 23.4 to 11.8 m²/g and their mean sizes increased from 47.8 to 94.7 nm, respectively. The saturation magnetizations of the powders changed from 32 to 44 emu/g according to changes in the post-treatment temperatures. The coercivities of the powders post-treated at temperatures of 700 and 800°C were 118 and 130 Oe, respectively.

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Key-words : Spray pyrolysis, Nickel ferrite, Nano powder

[Received October 22, 2008; Accepted April 16, 2009]

1. Introduction

Due to the extremely small sizes or large specific surface areas of nanomagnetic powders, they have unusual physical and chemical properties that are significantly different from those of conventional bulk materials.^{1)–3)} Nanomagnetic powder materials have been employed in many applications such as high-density magnetic recording and magnetic fluids for the storage and/or retrieval of information, magnetic resonance imaging (MRI) enhancement, catalysis, magnetically guided drug delivery, and sensors.^{4)–6)} Among various nanomagnetic powders, NiFe_2O_4 powder is one of the most important. In the past, various methods have been developed for preparing NiFe_2O_4 powders with desired properties, such as solid-state reactions, citrate precursor technique, coprecipitation, mechanical alloying, sol–gel method, shock wave technique, reverse micelle method, and a hydrothermal process.^{7)–13)}

Spray pyrolysis, an aerosol process, has been successfully applied to the preparation of ceramic powders, because it is a simple, inexpensive, and continuous process. It is also used to prepare ferrite materials. For example, González-Carreño et al. prepared barium ferrite nanopowders by spray pyrolysis.¹⁴⁾ Nanosized powders were directly prepared by aerosol pyrolysis from the citrate aqueous solution with low metal concentration of 0.02 M. Further, Li et al. investigated the effects of various combinations of chlorides and nitrates of manganese and iron on the morphology, phase, surface area, and magnetic properties of MnFe_2O_4 powders prepared by spray pyrolysis.¹⁵⁾ In addition, Yu and Gadalla prepared NiFe_2O_4 powders by spray pyrolysis and investigated the effects of operating parameters on the quality of the aerosol product.¹⁶⁾

In this study, NiFe_2O_4 powders with large-sized, hollow, and thin wall structures were directly prepared by spray pyrolysis from a spray solution containing an organic additive. After being

post-treated at high temperatures, these powders converted into nanosized NiFe_2O_4 powders. The mean sizes of the NiFe_2O_4 powders were controlled by changing the post-treatment temperatures. Effects of the post-treatment temperatures on the mean sizes, BET surface areas, saturation magnetizations, and coercivities of the NiFe_2O_4 powders were investigated.

2. Experiments

The schematic diagram of spray pyrolysis system used in this work is given elsewhere.¹⁷⁾ The system consists of droplet generator, quartz reactor, and powder collector. A 1.7 MHz ultrasonic spray generator having six vibrators was used to generate large amount of droplets, which are carried into the high-temperature tubular reactor by air as the carrier gas. The length and diameter of the quartz reactor are 1200 and 50 mm, respectively. Iron chloride and nickel chloride as starting materials were used. The overall concentration of Ni and Fe components was fixed at 0.2 M. The concentration of citric acid used as organic additive was 0.4 M. The flow rate of air used as carrier gas was 45 L/min. The as-prepared powders obtained by spray pyrolysis at 900°C were post-treated in a box furnace at a temperature between 600 and 1000°C for 2 h in air atmosphere to change the crystallinity and morphology.

The crystal structures of the as-prepared and post-treated NiFe_2O_4 powders were investigated by X-ray diffractometry (XRD; RIGAKU Co., DMAX-33). The morphological characteristics of the powders were investigated by scanning electron microscopy (SEM; JEOL Ltd., JSM 6060). Measurement of the thermal properties of the precursor powders was performed on a thermo-analyzer (TG-DSC; Netzsch, STA409C, Germany) in the temperature range from 40 to 900°C (10°C/min). Surface areas of the powders were measured by the Brunauer–Emmett–Teller (BET) method using N_2 as the adsorbate gas. The powder size was estimated from specific surface area assuming spherical shape. A vibrating sample magnetometer (VSM; 7300 Lake-shore, USA) was used to measure the saturation magnetization

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of the nickel ferrite powders as well as the coercive force.

3. Results and discussion

XRD patterns of as-prepared powders obtained by spray pyrolysis from spray solutions with and without citric acid are shown in **Fig. 1**. Addition of citric acid to the spray solution changed the crystal structures of the as-prepared powders obtained by spray pyrolysis. The powders prepared from the spray solution with citric acid were poorly crystallized and the main phase was spinel NiFe_2O_4 . On the other hand, the powders prepared from the spray solution without citric acid were mainly composed of nickel chloride hydrate and iron oxide phases. The differences between the phase compositions may be attributed to the formation of the citric acid chelates of Ni and Fe, which may change dried droplets to viscous melts. Evolution of gases in the decomposition of the chelates may inflate the droplets making the particles hollow.¹⁸⁾ The as-prepared powders by spray pyrolysis from the spray solution with citric acid had broad XRD peaks, which may be attributed to the short residence time (0.45 s) of the powders inside the reactor.

Figure 2 shows TG/DSC curves of the as-prepared powders obtained by spray pyrolysis from the spray solutions with and without citric acid. The TG curve of the powders prepared from

Fig. 1. XRD patterns of as-prepared powders obtained from the spray solutions with and without citric acid.

Fig. 2. TG/DSC curves of as-prepared powders obtained from the spray solutions with and without citric acid: (a) No additive, (b) 0.4 M CA.

(a) No additive

(b) 0.4 M CA

Fig. 3. SEM images of as-prepared powders obtained from the spray solutions with and without citric acid.

(a) 600°C

(b) 1000°C

Fig. 4. SEM images of post-treated NiFe_2O_4 powders obtained from the spray solution without citric acid.

the spray solution without citric acid shows two weight losses at temperatures below 800°C. The first pronounced weight loss region below 200°C is related to the decomposition of the Fe precursor. The second weight loss region from 450 to 700°C is related to the decomposition of the Ni precursor. Because of the short residence time of the powders, complete decomposition of the reactant precursors did not occur in the spray pyrolysis process. On the other hand, in the TG curve of the powders prepared from the spray solution with citric acid, rapid weight loss was not observed. A small weight loss of the powders occurred below 800°C due to the burning out of the residual carbon contaminant. The total weight losses of the powders prepared from the spray solutions with and without citric acid were 7.5 and 28.1%, respectively.

Figure 3 shows the SEM images of the as-prepared powders obtained by spray pyrolysis from the spray solutions with and without citric acid. The powders prepared from the spray solution without citric acid had bimodal size distributions with nanometer and micrometer sizes. Nickel chloride used as the source material of the Ni component had high volatility at a temperature of 900°C. Therefore, some of the nickel chloride precursor may be evaporated inside the reactor before being decomposed into NiO. The evaporated vapors of the nickel chloride precursor formed nanosized powders by the chemical vapor deposition (CVD) process. Powders with micrometer sizes had spherical shapes. However, those prepared from the spray solution with citric acid had sizes of the order of several micrometers, and their structures were hollow. Evolution of gas by the decom-

Fig. 5. SEM images of post-treated NiFe_2O_4 powders obtained from the spray solution with citric acid.

Fig. 6. XRD patterns of NiFe₂O₄ powders post-treated at various temperatures.

Table 1. Characteristics of the NiFe₂O₄ Powders Post-treated at Various Temperatures

Post-treatment temperature(°C)	Surface area (m ² /g)	Mean powder size (nm)	Saturation magnetization (M _s)(emu/g)	Coercivity (H _c)(Oersted)
600	14	79.8	32	279
700	23.4	47.8	40	118
800	17.1	65.3	40.5	130
900	16	69.9	42.5	133
1000	11.8	94.7	44.1	110

Fig. 7. Hysteresis curves of NiFe₂O₄ powders post-treated at various temperatures.

position of citric acid added to the spray solution resulted in powders with hollow structures. The problem of evaporation of nickel chloride was solved by the addition of citric acid to the spray solution by forming the chelates of Fe and Ni components.

Figure 4 shows SEM images of post-treated NiFe₂O₄ powders obtained from the spray solution without citric acid. The as-prepared powders obtained by spray pyrolysis from the spray solution without citric acid were post-treated at temperatures of

600 and 1000°C. The post-treated NiFe₂O₄ powders had hollow and aggregated structure of the nanometer size primary powders.

Micron sized NiFe₂O₄ powders turned to the nano-sized powders by weak press. **Figure 5** shows SEM images of the pressed NiFe₂O₄ powders. The post-treated powders with spherical shapes converted into nanosized powders. Irrespective of the post-treatment temperatures, the post-treated NiFe₂O₄ powders had nanometer sizes.

Figure 6 shows XRD patterns of the post-treated NiFe₂O₄ powders. The powders post-treated at a temperature of 600°C had a small impurity peak attributed to Fe₂O₃. However, phase-pure NiFe₂O₄ powders were obtained at post-treatment temperatures between 700 and 1000°C. The mean crystallite sizes of the NiFe₂O₄ powders calculated from the peak width of the XRD patterns by Scherrer's equation increased from 29 to 45 nm when the post-treatment temperature was changed from 600 to 1000°C, respectively.

The BET surface areas and mean powder sizes calculated from the BET surface areas are shown in **Table 1**. The BET surface areas of the NiFe₂O₄ powders decreased from 23.4 to 11.8 m²/g when the post-treatment temperatures were increased from 700 to 1000°C. Therefore, the average particle sizes of the powders increased from 47.8 to 94.7 nm when the post-treatment temperatures were increased from 700 to 1000°C, respectively.

Hysteresis loops of all samples were measured at room temperature. Typical loops for NiFe₂O₄ powders post-treated at different temperatures are shown in **Fig. 7**. The saturation magnetizations and coercivities of the powders post-treated at temperatures between 600 and 1000°C are given in Table 1. The post-treated powders show smooth hysteresis loops, which confirm the formation of pure nickel ferrite. The saturation magnetizations of the NiFe₂O₄ powders changed from 32 to 44 emu/g according to changes in the post-treatment temperatures. The increase in the powder size caused an increase in the saturation magnetization; this behavior is in good agreement with the result¹⁹⁾ obtained by Morrison and Haneda. The coercivities of the powders changed from 110 to 133 Oe when the post-treatment temperatures were changed from 700 to 1000°C.

4. Conclusions

Powders prepared by spray pyrolysis from the spray solution without citric acid had bimodal size distributions with nanometer and micrometer sizes. The post-treated NiFe₂O₄ powders obtained from the spray solution with citric acid had nanometer sizes and regular morphology. The mean sizes of the nanosized NiFe₂O₄ powders were controlled by changing the post-treatment temperatures. The saturation magnetizations and coercivities of the nanosized powders were affected by the post-treatment temperatures.

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