Novel Method to Synthesize Nanosized ZnFe_2O_4 Powders

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パルス細線放電法による ZnFe_2O_4 超微粒子の作製

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Nanocrystalline zinc ferrite (ZnFe_2O_4) powders have been synthesized successfully by high power, short pulse, electric discharge using Fe and Zn wires in oxygen gas. The powders were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Mean size of the particles obtained was determined by both BET and TEM was 12–56 nm depending on the oxygen pressure. XRD analysis shows that the zinc ferrite spinel was clearly obtained. [Received January 31, 2005; Accepted August 19, 2005]

Key-words : Zinc ferrite, Spinel, Nanopowders, Pulsed wire discharge

1. Introduction

Zinc ferrite (ZnFe_2O_4) has a normal spinel structure with a tetrahedral A-site occupied by Zn^{2+} ions and octahedral B-site by Fe^{3+} ions.¹⁾ Recently, this material is widely used in various fields of industries including magnetic materials, gas sensors, semiconductive photocatalysts and medicines.^{2)–7)} The properties of ZnFe_2O_4 in above applications are highly affected by the particle size. It has been indicated that nanocrystalline ZnFe_2O_4 is especially good for the promotion of properties. Various methods, including sol-gel routes,⁸⁾ chemical coprecipitation,⁹⁾ hydrothermal synthesis,¹⁰⁾ thermal plasma synthesis¹¹⁾ and microemulsion method,¹²⁾ have been developed to synthesize ZnFe_2O_4 nanocrystalline powders. Generally, chemical methods can produce nanopowders at high production rates, but particle agglomeration has often been observed and extreme heat treatment to crystallize the powders is essential. However, that of the production rate and controlling composition by conventional physical methods is unsatisfactory. Pulsed wire discharge (PWD) method is a novel method for the production of nanosized materials^{13),14)} due to the high quenching rate of high temperature and high density plasma, which is favorable for producing fine particles. Previously, NiFe_2O_4 nanosized powders were successfully synthesized by PWD.^{15)–17)} However, no attempts have been reported on the synthesis of ZnFe_2O_4 powders. In the present work, nanocrystalline ZnFe_2O_4 particles are synthesized by PWD method and the microstructure and composition of the particles are analyzed.

2. Experiments

Synthesis of ZnFe_2O_4 nanoparticle by PWD method was carried out on a pulsed discharge facility. The experimental set up is shown in Fig. 1. A pulsed high current was driven through twisted iron and zinc wires. The length of the twisted wires was 25 mm, and the diameter of Fe wire was 0.3 mm. The diameter of Zn wire was controlled by polishing the wire to 0.24 mm to fit the molar ratio of Zn and Fe as 1 : 2. The wires were connected with electrodes in a chamber that was filled with oxygen gas at pressures of 13.3–106.4 kPa. Electrodes were connected to a capacitor of 30 μF through a gap switch. The capacitor was charged at a voltage of 6 kV, and a current was generated through the twisted wires by closing the

Fig. 1. Experiment setup.

gap switch. Typical pulse width and discharge repetition rate was 10 to 20 μs and 0.2 Hz, respectively. The wires were melted, evaporated and ionized by Joule's heat to form plasma. Then the plasma expands in the surrounding oxygen gas, following the collision and reaction with oxygen atoms. The plasma was gradually cooled down in a nature manner to form ultrafine particles. Particles suspended in the chamber were collected by pumping the oxygen gas through a membrane filter. Specific surface area of the synthesized powders was measured with a Brunauer-Emmet-Teller (BET) apparatus (Flowsorb 2300, Shimadzu Co.) using N_2 adsorption. From the measured specific surface area of the synthesized powders, average grain size was estimated assuming that all the particles were spherical and stoichiometric ZnFe_2O_4 grains. Phases of powders were identified by powder X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation, $\lambda = 0.154056$ nm. The morphology and size distribution of the synthesized powders was observed by

Fig. 2. XRD patterns of ZnFe_2O_4 nanocrystallites synthesized at different oxygen pressure.

transmission electron microscopy (TEM).

3. Results and discussion

The XRD patterns for the collected particles synthesized at different oxygen pressure are shown in Fig. 2. Most of the peak positions matched with that of the ICDD powder diffraction data for ZnFe_2O_4 (Franklinite, 22-1012). The presence of distinct XRD peaks indicates that a single crystalline phase was obtained. Two small peaks located near 2θ of 31.8° and 36.1° are associated with ZnO. With the increase in oxygen pressure, the relative intensity of ZnO peaks was apparently reduced. At 106.4 kPa, ZnO phases were further reduced, almost no ZnO phases in the powders were detected. It indicates that the ZnFe_2O_4 spinel formation benefited from higher oxygen partial pressure. Similar results are also reported by Li et al.¹⁸⁾ and Peng et al.¹⁹⁾ During PWD processing, it has been noted that the vapor is compressed into a smaller volume by the ambient gas at higher pressure during discharge, as described by Suzuki et al.²⁰⁾ Relatively high-density plasma in compressed vapor may enhance the chemical reaction via the high frequency atoms collision to form the complex oxide.

Figure 3 shows the specific surface area measured by BET as a function of oxygen pressure. Average particle size increased with increasing oxygen partial pressure. At 13.3 kPa, the mean particle size was estimated about 12 nm, while at 106.4 kPa, the particle size increased to about 56 nm. It seems that the high frequency collisions between atoms in the vapor at higher pressure have both merits, i.e. formation of high purity ZnFe_2O_4 , and demerits, i.e. formation of larger sized particle. The latter is a typical phenomenon of PWD.¹⁶⁾

Figure 4 shows the TEM image of ZnFe_2O_4 nanocrystallites synthesized at 13.3 kPa O_2 pressure. From Fig. 4, they are monodisperse and ultrafine particles. Circular or hexagonal grains with size between 5 to 50 nm in diameter can be seen in the micrograph. Meanwhile, all the diffraction rings appearing in this pattern can be identified as reflections from ZnFe_2O_4 phase.

In most synthesis processes for MFe_2O_4 (M: Ni, Zn, Mg, Co...), it often require extra-heat treatment to crystallize the obtained particles,^{8)-10),12)} which may result in the grain growth during heat treatment.²¹⁾ Furthermore, the inconvenient synthesis process as well as the particles cohesion restricted their practical applications. In this study, ZnFe_2O_4 nanocrystallites were synthesized directly via a gas phase reaction without any extra-treatment. Particle size can be con-

Fig. 3. Specific surface area and mean particle size as a function of gas pressure.

Fig. 4. TEM bright field image of ZnFe_2O_4 nanocrystallites.

trolled easily by controlling the oxygen pressure. Moreover, there is no obvious particle agglomeration in the synthesized powders, which is important for most practical industrial applications. Nevertheless, like most of the physical synthesis methods, the powder production rate in the present study was relatively lower than that of the chemical methods. This demerit can be overcome by increasing the discharge repetition rate, which will be an important aspect of future work in regard to commercial application of this method.

4. Conclusion

Nanopowders of ZnFe_2O_4 were successfully prepared by pulsed wire discharge in oxygen. The powders were monodispersed. The average powder size and composition were strongly influenced by the oxygen pressure. High oxygen pressure caused an increase in powder size, and the formation of other compounds, such as ZnO was effectively controlled. When the oxygen pressure was raised to 106.4 kPa, almost no ZnO composition could be detected.

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