Nanosized Ferrite Particles Synthesized by Pulsed Wire Discharge

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Ultrafine ferrite particles have significant potential for many applications, such as magnetic recording media, ferrofluids, radar-absorbing coatings, and targeted drug delivery. Various methods have been developed for these applications. However, many of these applications require particles of predetermined size and narrow size distribution. Chemical methods cannot well satisfy these requirements since the particles size distribution is affected by the synthesis temperature and temperature distribution. Development of more effective method that lead to particles with these characteristics are therefore of considerable interest.

Pulsed wire discharge (PWD) method is a novel method for the production of nanosized materials due to the easily achievable high temperature and energy densities and high quenching rate, which are favorable for producing fine particles. In the present work, this method was employed to synthesize zinc ferrite (ZnFe_2O_4) and Cobalt ferrite (CoFe_2O_4).

Figure 1 shows the specific surface area measured by BET and the calculated mean particles size as a function of oxygen pressure. Mean particles size was increased with increasing oxygen partial pressure for both kinds. At 13.3 kPa, the mean particles size was

estimated about 12 nm and 20 nm for ZnFe_2O_4 and CoFe_2O_4 powders, respectively. At 53.3 kPa, on the other hand, the mean size of two kinds increased to about 40~50 nm. It seems that the higher frequency collisions between atoms in the vapor at higher pressure have both merit, i.e. to form high purity magnetic ferrites and reduce the formation of other oxides compounds, such as ZnO and CoO. However, there is a demerit, i.e. to form larger sized particles in higher pressure.

The Typical TEM image of the ZnFe_2O_4 nanocrystallites synthesized at 13.3 kPa O_2 pressure is shown in Fig. 2. From Fig.2, we see monodisperse and ultrafine particles. This is one of the important features from the particles synthesized by chemical method, where the particles synthesized often shows particles agglomerated particles. Spherical grains with very uniform size distribution, more than 85% of the particles are in the range of 5 to 30 nm in diameter. The electron diffraction shows that almost all the diffraction rings appearing were identified as reflections from ZnFe_2O_4 phase.

Fig. 1. Dependence of the specific surface area and the mean particle size of the gas pressure; For Zn-Fe-O (●,○) and Co-Fe-O (▲,△)

Fig. 2. TEM micrograph of the ZnFe_2O_4 nano crystallites

Nanosized Ferrite Particles Synthesized by Pulsed Wire Discharge

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Nanocrystallites ferrite particles (ZnFe_2O_4 , CoFe_2O_4) have been synthesized successfully by high power short electric pulse discharge of Fe and metal wires in oxygen. The powders were characterized by X-ray diffraction (XRD) and transmission electron microscopy (TEM). Mean size of the obtained particles strongly depended on the oxygen pressure, which were determined by both BET and TEM. TEM observation shows that the well dispersed, uniform sized ferrite nanocrystallites was synthesized.

Keywords: pulsed wire discharge, ultrafine particles, spinel

1. Introduction

Ultrafine ferrite particles have significant potential for many applications, such as magnetic recording media, ferrofluids, radar-absorbing coatings⁽¹⁾⁽²⁾, and targeted drug delivery⁽³⁾⁽⁴⁾. Chemical precipitation and coprecipitation are the economical routes for the production of large quantities of fine/ultrafine ferrite particles⁽⁵⁾. However, many of these applications require particles of predetermined size and narrow size distribution. Chemical methods cannot well satisfy these requirements since the particles size distribution is affected by the synthesis temperature and temperature distribution. Development of more effective method that lead to particles with these characteristics are therefore of considerable interest. Microemulsion, crystallization from glass, freeze-drying, sol-gel, plasma and other physical methods was developed⁽¹⁾⁽⁶⁾⁽⁷⁾. Pulsed wire discharge (PWD) method, which was invented by Jiang et al⁽⁸⁾, is a novel method for the production of nanosized materials due to the easily achievable high temperature and energy densities and high quenching rate, which are favorable for producing fine particles. In the previous work, this method has been applied to synthesize metal or ceramic nanopowders. Most of these are based on monoelemental metal wire discharge in various gases. If we apply dual elemental metal wire discharge in gas, it is also possible to synthesize alloys and complex oxide ceramic nanopowders. However, to synthesize complex oxides or alloys often need double wires or even multi-wires discharge in gas simultaneously, which may result in different synthesis products if the discharge condition is changed. Experimentally, NiO and iron oxides have been observed in the synthesized powders⁽⁹⁾. Therefore, controlling the synthesis condition is extremely important for the ultimate products. A further experiment to investigate the relation of powders composition with the discharge condition is necessary.

Since zinc ferrite (ZnFe_2O_4) has a normal spinel structure, it is of interest not only from basic research in magnetism, but also has great potential in technological applications, such as gas sensor

and semiconductor photocatalyst⁽¹⁰⁾⁽¹⁴⁾. Cobalt ferrite (CoFe_2O_4) is another ferrite for hard magnetic applications. In fact, Co modified maghemite is widely used for magnetic recording media. The properties of these materials in above applications are highly affected by the particle size, and nanocrystalline particles is especially good for the property promotion. In order to reveal the effects of synthesis condition on the composition and structure of the powders, the nanocrystalline ZnFe_2O_4 and CoFe_2O_4 particles are synthesized by PWD method in this work, and the microstructure and composition of the particles are analyzed.

2. Experimental Procedure

Synthesis of ferrite ultrafine particle by PWD method was carried out on a pulse 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 molar ratio of Zn (Co) and Fe was controlled to 1:2 by controlling the diameter of the wires. The wires were connected with electrodes in a chamber that was filled with oxygen gas at pressures of 13.3–53.3 kPa. Electrodes were also connected to a capacitor bank through a gap switch. The capacitor was charged at the voltage of 6 kV, and pulsed current was fed through the twisted wires by closing the gap switch. Typical pulse width and discharge repetition was 10 to 20 μs and 0.2 Hz, respectively. The wires were melted, evaporated and ionized by the Joule's heating to plasma. The plasma vapor expanded in the surround oxygen gas, following the collision and reaction with oxygen atoms to form ultrafine particles by rapid cooling. Particles floating in the chamber were collected by pumping the oxygen gas through a membrane filter. Specific surface area of synthesized powders was measured by Brunauer-Emmet-Teller (BET) method (Flowsorb 2300, Shimadzu) 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, stoichiometric, and deflocculated grains. Phases of the powders were identified by powder X-ray diffraction (XRD) using Cu K α radiation, ($\lambda=0.154056\text{ nm}$). The morphology and size distribution of the synthesized powders was observed by transmission electron microscope (TEM).

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Fig. 1. Experiment setup

3. Results and Discussion

The XRD patterns for the collected particles synthesized at different oxygen pressure are shown in Fig. 2. In the Zn-Fe-O system, most of the peak positions matched with that of the joint committee on powder diffraction standards (JCPDS) powder diffraction data for ZnFe_2O_4 , as shown in Fig. 2 (a). The presence of distinct XRD peaks indicates that a single crystalline phase was obtained. Two small peaks located near at $2\theta = 31.8^\circ$ and 36.1° are associated with zinc oxide. The intensity of these two peaks strongly depended on the oxygen pressure. The relative intensity of ZnO peaks was apparently reduced with increasing oxygen pressure. The volume fraction of zinc oxide can be calculated by calculation the peak area ratio of ZnO ($2\theta = 31.8^\circ$) and ZnFe_2O_4 (peak 311). The results shows that less than 2 vol% of zinc oxide in the powders was contained, when synthesized at 53.3 kPa pressure. The same phenomenon was also observed in the Co-Fe-O system, as shown in Fig. 2 (b). CoFe_2O_4 peaks were clearly shown in this pattern. A little amount of CoO was detected for all the powders regardless the oxygen pressure, but it was obviously reduced at higher oxygen pressure. This indicates that the compressed vapor formed by higher oxygen atmosphere may enhance the chemical reaction to form ZnFe_2O_4 and CoFe_2O_4 spinel.

Figure 3 shows the specific surface area measured by BET and the calculated mean particles size as a function of oxygen pressure. Mean particles size was increased with increasing oxygen partial pressure for both kinds. At 13.3 kPa, the mean particles size was estimated about 12 nm and 20 nm for ZnFe_2O_4 and CoFe_2O_4 powders, respectively. At 53.3 kPa, on the other hand, the mean size of two kinds increased to about 40~50 nm. It seems that the higher frequency collisions between atoms in the vapor at higher pressure have both merit, i.e. to form high purity magnetic ferrites and reduce the formation of other oxides compounds, such as ZnO and CoO. However, there is a demerit, i.e. to form larger sized particles in higher pressure.

The TEM image of the ZnFe_2O_4 nanocrystallites synthesized at 13.3 kPa O_2 pressure is shown in Fig. 4. From Fig.4, we can see monodisperse and ultrafine particles. This is one of the important

Fig. 2. XRD patterns of (a) ZnFe_2O_4 and (b) CoFe_2O_4 nano-particles synthesized at different oxygen pressure

Fig. 3. Dependence of the mean particle size and the specific surface area on the gas pressure ; For Zn-Fe-O (●,○) and Co-Fe-O (▲,△)

Fig. 4. TEM micrograph of the ZnFe_2O_4 nano crystallites

Fig. 5. Size distribution of the ZnFe_2O_4 nanocrystallites obtained from TEM image

features from the particles synthesized by chemical method, where the particles synthesized often shows agglomerated particles. Spherical grains with very uniform size distribution and the mean particle size around 10 nm can be seen in Fig. 4. Almost all the diffraction rings appearing in the electron diffraction also shown in Fig. 4 were identified as reflections from ZnFe_2O_4 phase.

The particles size distribution obtained from TEM image is shown in Fig. 5. It can be observed that more than 85 % of the particles are in the range of 5 to 30 nm in diameter, which is in good with that of the BET calculation. The narrow particles size distribution is another important features of PWD method from other chemical synthesis methods, since the gas phase synthesis is more easily to reach the temperature uniform than that of the liquid and solid phase methods.

4. Conclusion

In this work, a new preparation method has been developed for synthesis of ultrafine ZnFe_2O_4 and CoFe_2O_4 nanosized powders. The obtained particles were monodispersed, and particle size and composition were easily controlled by the discharge condition and oxygen pressure, which is important for preparation high quality nanosized magnetic powders for special applications. It seems that this new method is applicable to the synthesis of ultrafine magnetic ferrite particles.

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