Journal of Korean Association of Crystal Growth
Vol. 7, No. 1 (1997) 167-173

Synthesis and characterization of the ultrafine $ZnFe_2O_4$ powder by glycothermal

Dong-Sik Bae, Kyong-Sop Han, Seung-Beom Cho** and Sang-Hael Choi*
Division of Ceramics, Korea Institute of Science and Technology, Seoul 136-791, Korea
**Department of Inorganic. Materials. Engineering, Hanyang University, Seoul 133-791, Korea*
***Division of Materials Research Center, Rutgers University, U.S.A.*

Glycothermal에 의한 초미립의 $ZnFe_2O_4$ 분말 합성 및 특성

배동식, 한경섭, 조승범**, 최상훌*
한국과학기술연구원 세라믹스연구부, 서울, 136-791
*한양대학교 무기재료공학과, 서울, 133-791
**Rutgers대학교 세라믹센터, 미국

Abstract The $ZnFe_2O_4$ powder was prepared under glycothermal conditions by precipitation from metal nitrates with aqueous potassium hydroxide. The fine powder was obtained at temperatures as low as 225 to 300℃. The microstructure and phase of the $ZnFe_2O_4$ powder were studied by SEM and XRD. The properties of the powder were studied as a function of various parameters (reaction temperature, reaction time, solid loading, etc). The average particle size of the $ZnFe_2O_4$ increased with increasing reaction temperature. After glycothermal treatment at 270℃ for 8 h, the average particle diameter of the $ZnFe_2O_4$ was about 50 nm.

요 약 $ZnFe_2O_4$ 분말은 금속 질산염을 수산화 칼슘으로 침전시켜 이를 1,4-부탄에디올 속에서 비교적 고온고압을 가하여 얻어졌다. 미분말이 얻어진 온도는 225-300℃, 압력은 1-3.5 MPa이였다. 분말의 미세구조는 주사전자현미경으로 결정상은 X-선 회절 분석으로 행하였다. 분말의 물성과 반응온도, 반응시간 및 농도의 관계를 조사하였다. $ZnFe_2O_4$ 분말의 평균입자 크기는 반응온도와 시간이 증가함에 따라 증가하였다. 270℃에서 8시간 반응을 행한 경우의 평균입자 크기는 약 50 nm였다.

1. Introduction

Ferrites are a group of technologically important materials which are used in the fabrication of microwave devices. Spinel ferrites can be prepared by solid-state, evaporative decomposition of solutions (EDS), hydrolysis of metal organics, decomposition of metal organic solution, solid-solution precursor, and wet methods [1].

In using fine magnetic particles, particle size is the most important parameter, as are other qualities, such as crystallinity and composition, since the magnetic properties of the particles are strongly influenced by these properties. Therefore, it is advantageous that the particles are formed uniformly in size and shapemonodisperse or in a narrow size distribution in the desired size ranges. The preparation of colloidal particles with a narrow size distribution has been investigated by colloid chemists for a long time [2]. According to their theory, to produce colloidal particles with a narrow size distribution, the nucleation and growth process must be carefully controlled.

Hydrothermal synthesis meets the increasing demand for the direct preparation of crystalline ceramic powders and offers a low temperature alternative to conventional powder synthesis technique in the production of anhydrous oxide powders. This technique can produce fine, high purity, stoichiometric particles of single and multicomponent metal oxides [3]. Some precipitated hydroxides subjected to prolonged boiling under atmospheric pressure in their mother liquor or hydrothermally treated under enhanced pressure at elevated temperatures transform to fine-grained oxides of narrow particle size distribution. It has been demonstrated that such powders are composed of much softer agglomerates and sinter much better than those prepared by calcination decomposition of the same oxides [4]. These powders could be sintered at low temperature without calcination and milling steps [5,6].

Furthermore, if the process conditions su-ch as solution pH, solute concentration, reaction temperature, reaction time, seed materials, and the type of solvent are carefully controlled, ceramic particles of the desired shape and size can be produced [7].

The objectives of this study were to prepare ultrafine zinc ferrites using KOH under mild hydrothermal conditions.

2. Experimental procedure

The process for preparing $ZnFe_2O_4$ by glycothermal treatment in 1,4-butanediol solution is schematically illustrated in Fig. 1. $ZnFe_2O_4$ precursors were precipitated from 2 M $Fe(NO_3)_3 \cdot 9H_2O$ solution and 1 M $Zn(NO_3)_2 \cdot 6H_2O$ solution by slowly adding 1 M KOH solution with rapid stirring. The precipitated $ZnFe_2O_4$ precursors were washed by repeated cycles of centrifugation and redispersion in deionized water. Washing was performed for a minimum

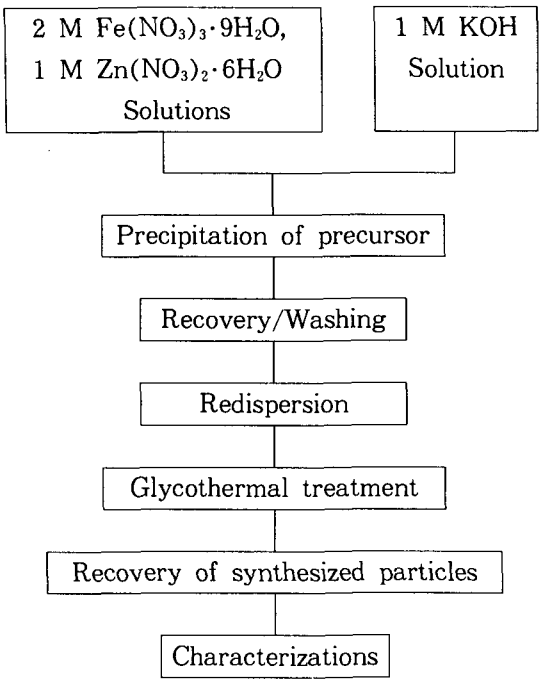

Fig. 1. Preparative procedure for the preparation of the $ZnFe_2O_4$ particles in 1,4-butanediol solution.

of five times each in deionized water and methanol. Execss solution was decanted after the final washing and the wet precursor was redispersed in 250 ml 1,4-butanediol under vigorous stirring. The resulting suspension was placed in a 1000 ml stainless steel pressure vessel, equipped with a magnetically stirred head. The vessel was then heated to the desired temperature at a rate of 10℃/min. Reaction conditions such as reaction temperature, reaction time, stirring speed, amount of methanol, and solid loading are listed in Table 1. During heating, the autogenous pressure gradually increased to 1 MPa and was usually maintained below 3.5 MPa during the holding period. After the treatment, the vessel was cooled to ~100℃ and any excess prressure relieved via a pressure release valve. The reaction products were washed at least five times by repeated cycles of centrifugation and redispersion is isopropanol. After washing, the recovered powders were dried at 100 ℃ in a desiccator for 24 h. The dried, recovered powders were analyzed for phase composition using X-ray diffraction (Phillips, PW 1825/00) over the 2 theta range from 10-70°at rate of 2.5°/min. The morphology of the synthesized particles was observed using scanning electron microscopy (SEM, Hitachi S-4200). The analysis of the surface area of the synthesized powder was performed by gas adsorption-desorption (Micromeritis, ASAP 2000) studies using N_2 at 77 K.

3. Results and discussion

A nucleation and growth process often determines the process temperature and process time, the particle size and the chemical phase development in ceramic powder synthesis. Their growth mechanism can be summarized as follows: (1) dissolution of the starting materials, (2) transport of the Zn, Fe in the hydrothermal fluid, (3) nucleation of the Zn ferrite followed by isotropic growth. Therefore, all growth steps are affected by the chemistry of the hydrothermal medium, hence by the additive present: the dissolution step (control of the

Table 1
Synthesis conditions of the $ZnFe_2O_4$ in 1,4-butanediol solution

Sample No.	Reaction temperature (℃)	Reaction time (h)	Amount of methanol (ml)	Solid loading (g/200 ml)
1	225	10	no	10
2	250	10	no	10
3	270	10	no	10
4	270	16	no	10
5	300	10	no	10
6	270	5	no	10
7	270	10	no	20
8	270	10	no	5
9	270	10	30	10

metal solubility and supersaturation), the transport step (formation of metal-additive soluble complex species), and the nucleation-growth step (adsorption on selected surfaces). Figure 2 shows the scanning electron micrographs of the synthesized $ZnFe_2O_4$ powders. All the $ZnFe_2O_4$ powders were synthesized at 225 to 300℃. Glycothermal synthesis of the $ZnFe_2O_4$ from nitrates in KOH led to somewhat nearly spherical and ultrafine particles which were on the order of 40 to 75 nm in size. KOH appears to act as a morphological catalyst during these hydrothermal synthesis and hence approximately spherical $ZnFe_2O_4$ particles resulted. The sharp diffraction peaks consistant with the well defined and crystallized particles shown Fig. 3. The transformation of precursor to $ZnFe_2O_4$ in 1,4-butanediol did occur in the range of 225 to 300℃ and 1 to 3.5 MPa, respectively. The morphology formed are extremely uniform in particle size. The reaction temperature has an effect on the size of the $ZnFe_2O_4$ particles synthesized in 1,4-butanediol solution (Fig. 4). The temperature had a great effect on the grain size of the products and the agglomeration among grains. Lowering temperature will give rise to decreasing grain size and increasing agglomeration among grains. Increasing reaction temperatures changes the size of the $ZnFe_2O_4$ particles. The $ZnFe_2O_4$ particles with higher reaction temperatures have larger spherical shape. Figure 5 shows the effect of the solid loading on the average size of the $ZnFe_2O_4$ particles. The effect of the solid loading on the size of the $ZnFe_2O_4$ particles, increasing the solid loading changes the size of the $ZnFe_2O_4$ from 45 to 75 nm. As seen in Equation (1) below, since nucleation frequency (N) is related to temperature, free energy, and nucleation rate (J_s), nuclea-

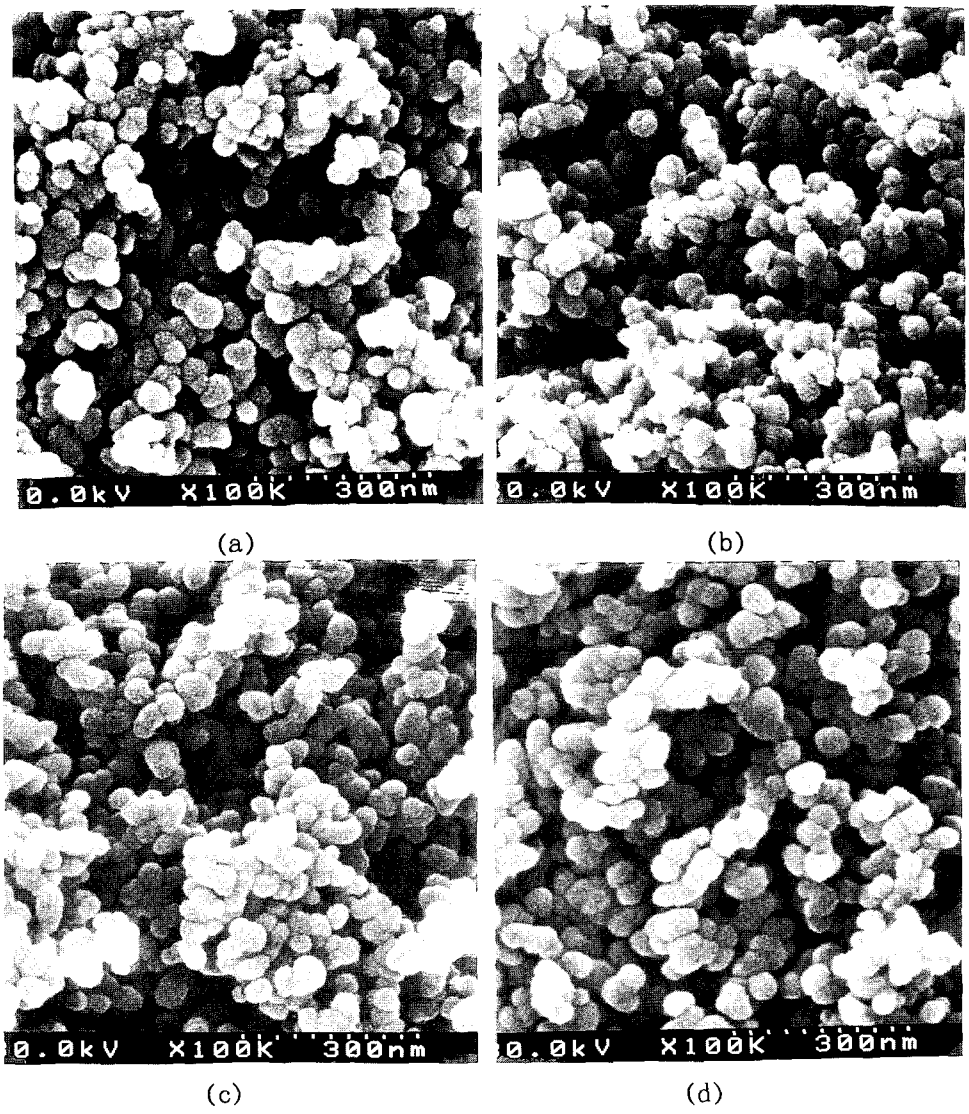

Fig. 2. SEM photomicrographs of the $ZnFe_2O_4$ particles synthesized by glycothermal treatment as a function of reaction temperature at : (a) 225℃, (b) 250℃, (c) 270℃ and (d) 300℃.

tion number is the same in both cases and increasing the solid loading increases the size of the $ZnFe_2O_4$ particles [8,9].

$$J_s=Z\beta N\exp(-\triangle G/kT) \quad (1)$$

where J_s is the steady-state nucleation rate, Z a nonequilibrium factor (constant), β a diffusion factor (constant), N the number of nucleation sites/volume, and $\triangle$ G, k, and T have their usual meanings.

Thus, the hydrothermal method used

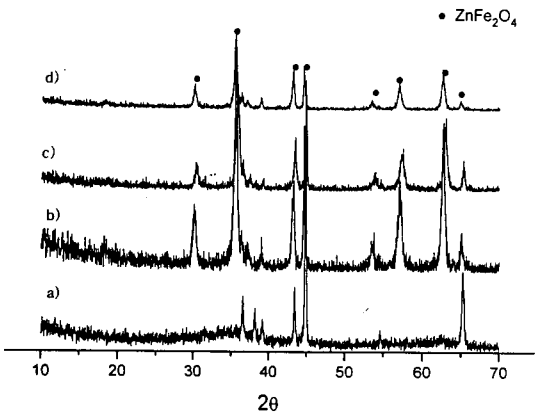

Fig. 3. X-ray diffraction pattern of the $ZnFe_2O_4$ particles synthesized by glycothermal treatment;(a) raw materials, (b) 250 ℃, (c) 275℃ and (d) 300℃.

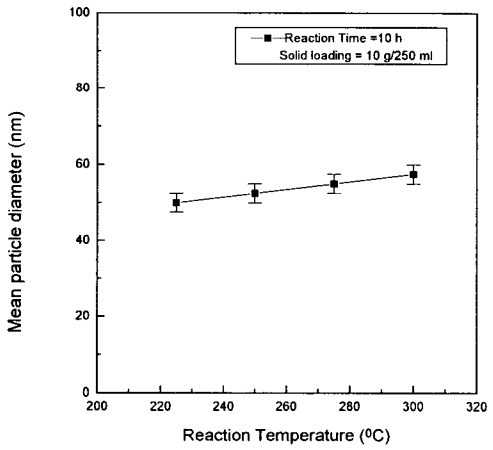

Fig. 4. Mean particle diameter of the $ZnFe_2O_4$ particles vs. Reaction temperature.

here led to ultrafine spherical particles which may be useful for several applications such as in the preparation of ferrite coatings.

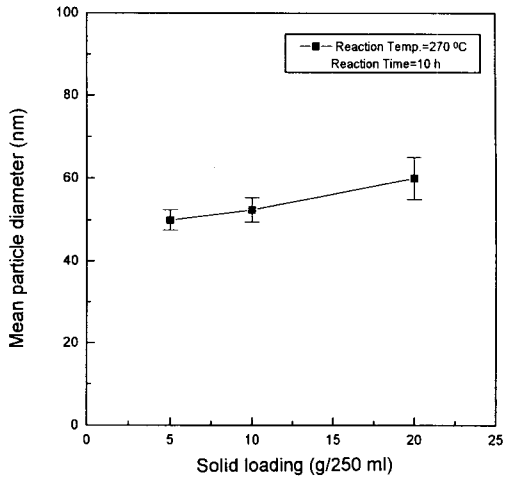

Fig. 5. Mean particle diameter of the $ZnFe_2O_4$ particles vs. solid loading.

4. Conclusions

Ultrafine, nearly spherical, and high purity ferrites of several compositions including solid solutions can be prepared by neutralizing the nitrate solutions in KOH under mild hydrothermal conditions.

After glycothermal treatment at 270℃ for 8 h, the average particle diameter of the $ZnFe_2O_4$ was about 50 nm. The average particle diameter of the $ZnFe_2O_4$ increased with increasing reaction temperature and time. The results of this study show that it is possible to control the size of the $ZnFe_2O_4$ particles glycothermally synthesized in 1,4-butanediol solution, if the synthesis conditions such as reaction temperatures and solid loading are carefully controlled.

References

[1] P.E. Matijevic, Colloid Science of Composite Systems, in Science of Ceramic Chemical Processing, Edited by L.L. Hench and D.R. Ulrich. (Wiley, New York, 1986) pp. 463-81.

[2] V.K. LaMer and R.H. Dinegar, J. Am. Chem. Soc. 72 (1950) 4847.

[3] S. Komarneni, E. Fregeau, E. Breval and R. Roy, J. Am. Ceram. Soc. 71 [1] C-26-C-28 (1988)

[4] K. Haberko and W. Pyda, Advances in Ceramics, Vol. 12, Science and Technology of Zirconia Ⅱ, Edited by N. Claussen, etc, (Am. Cera. Soc., 1984) pp. 774-83.

[5] M. Rozman, M. Drofenik and D. Kolar, Euro-Ceramics, Vol. 5 (1995) pp. 47-54.

[6] S. Komarneni, E. Freagan, E. Bravel and R. Roy, J. Am. Sci. 71[1] (1988), C-26-C-28.

[7] S.B. Cho, et al., Sci., Tech. & App., of Colloid. Susp., edited by J.H. Adair, J.A. Casey, C.A. Randall (Sridhar Venigalla, 1995) pp. 139-150.

[8] G.L. Messing, J.L. McArdle and R. A. Shelleman, in Materials Research Society Symposium Proceedings, Vol. 73, Better Ceramics Through Chemistry Ⅱ, Edited by C.J. Brinker, D. E. Clark and D.R. Ulrich (Materials Research Society, Pittsburgh, PA, 1986) pp. 471-80.

[9] R.A. Shelleman and G.L. Messing, J. Am. Ceram. Soc. 71 [5] (1988) 317-322.