Glycothermal Synthesis of Ultrafine $ZnFe_2O_4$ powder

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Abstract

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

Introduction

There has been considerable attention in improving the performance of ceramics in electronic and structural applications by careful control of median size, size distribution, and shape of the precursor powders[1-3].

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. Furthmore, if the process conditions such 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[4].

During the synthesis a nanosized ferrite powder with a narrow size distribution and large specific surface area is produced. These powders could be sintered at low temperature without calcination and milling steps[5-6].

Experimental Procedure

The process for preparing $ZnFe_2O_4$ by glycothermal treatment in 1,4-butanediol solution is schematically illustrated in Figure. 1. Zinc Iron hydrous oxide precursors were precipitated from 2M $Fe(NO_3)_3 \cdot 9H_2O$ solution and 1M $Zn(NO_3)_2 \cdot 6H_2O$ solution by slowly adding 1M KOH solution with rapid stirring.. The precipitated Znic Iron hydrous oxide precursors were washed by repeated cycles of centrifugation and redispersion in deionized water. Washing was performed for a minimum of five times each in deionized water and methanol. Execss solution was decanted after the final washing and the wet precursor was redispersed in 250ml 1,4-butanediol under vigorous stirring. The resulting suspension was placed in a 1000ml 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. During heating, the autogenous pressure gradually increased to 1MPa and was usually maintained below 3.5MPa during the holding period. 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 95℃ in a desiccator for 24hrs. The dried, recovered powders were analyzed for phase composition using X-ray diffraction(XRD) 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 micrpscopy(SEM).

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 metal solubility and supersaturation), the transport step(formation of metal-additive soluble complex species), and the nucleation-growth step(adsorption on selected surfaces).

A typical XRD pattern of the $ZnFe_2O_4$ particle synthesized in 1,4-butanediol solution is given in Figure. 2. The transformation of precursor to Zn ferrite in 1,4-butanediol did occur in the range between 225 and 300℃ and 1 and 3.5MPa. The sharp diffraction peaks consistant with the well defined and crystallized particles shown Figure. 3. 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. 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. 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 45nm to 75nm.

Conclusions

Glycothermal synthesis enables the preparation of Zinc ferrite powders with ultrafine. After glycothermal treatment at 270℃ for 8 hrs., 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. 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. T. Sugimoto, "Preparation of Monodispersed Colloidal Particles", Advan. Colloid. Interface Sci., 28, 65-108 (1987).

2. E. Matijevic, "Control of Powder Morphology", pp. 513-527, Chemical Processing of Advanced Materials, edited by L.L. Hench and J.K. West, John Wiley and Sons, Inc., 1992.

3. S. Somiya, Hydrothermal Reactions for Materials Science and Engineering: An Overview of Research in Japan, Elsevier Scinence Publishing Co., Inc., New York, NY, 1989.

4. S. B. Cho et al., "Morphological control of Alumina particles precipitated from 1,4-butanediol solution", pp. 139-150, Sci., Tech., & App., of Colloid. Susp., edited by James H. Adair, Jon A. Casey, Clive A. Randall, Sridhar Venigalla, 1995.

5. M. Rozman, M. Drofenik, D. Kolar, "Sintering of nanosized MnZn ferrite powders", Euro-Ceramics, vol. 5, pp. 47-54, 1995.

6. S. Komarneni, E. Freagan, E. Bravel, and R. Roy, "Hydrothermal preparation of Ultrafine Ferrites and their Sintering", J. Am. Sci., 71[1], (1988), C-26-C-28.

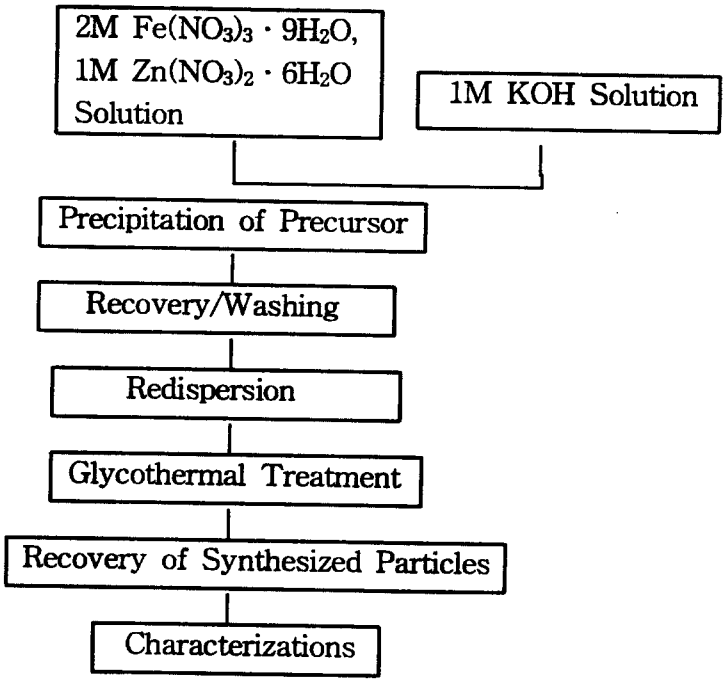

Fig. 1. Preparative procedure for the preparation of the $ZnFe_2O_4$ particles in 1,4-butanediol solution.

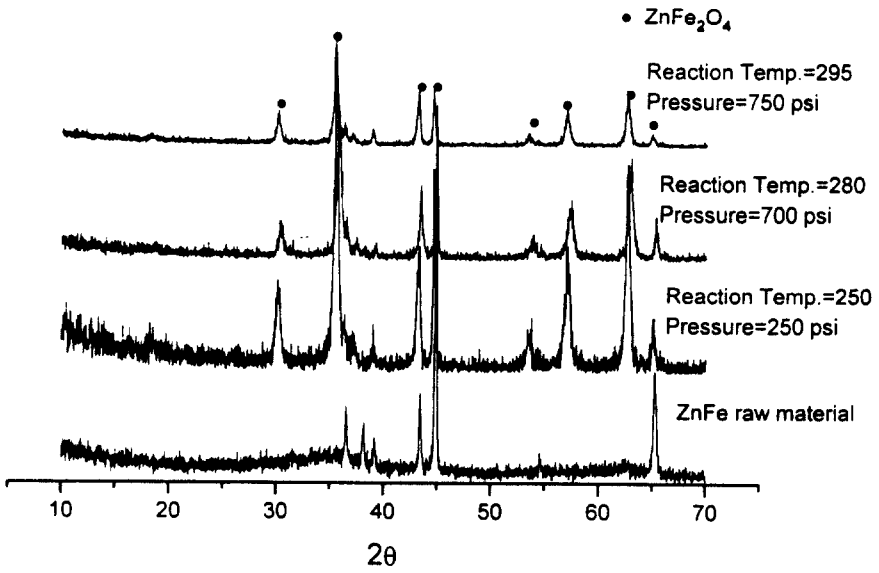

Fig. 2. X-ray diffraction pattern of the $ZnFe_2O_4$ particles synthesized by glycothermal treatment.

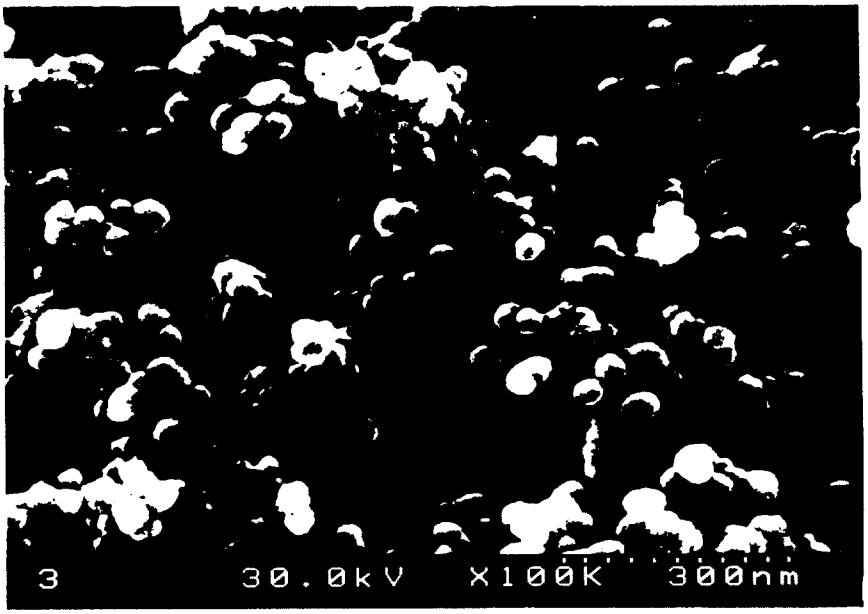

Fig. 3. SEM photomicrographs of the $ZnFe_2O_4$ particles synthesized with reaction temperature at 250℃ for 10 hrs.