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Fabrication of the ultrafine ZnO powder through glycothermal process

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Glycothermal 공정에 의한 미립 ZnO 분말의 제조

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Abstract The ZnO 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 275℃. The microstructure and phase of the powder were studied by SEM and XRD. The properties of the ZnO powder were studied as a function of various parameters (reaction temperature, reaction time, solid loading, etc). The average particle size of the ZnO increased with increasing reaction temperature. After glycothermal treatment at 225℃ for 8 h, the average particle size of the ZnO powder was about 150 nm and the particle size distribution was narrow.

요 약 고순도 ZnO 미분말은 금속 질산염을 수산화 칼슘으로 침전시켜 이를 1,4-부탄에디올속에서 고온고압 반응으로 얻어졌다. 이때 미분말이 얻어진 반응온도는 225-275℃, 압력은 1-3.0 MPa 이였다. 분말의 미세구조는 주사전자현미경으로 결정상은 X-선회절 분석으로 행하

였다. 분말의 물성과 반응온도, 반응시간 및 농도의 관계를 조사하였다. ZnO 분말의 평균입자 크기는 반응온도와 시간이 증가함에 따라 증가하고, 입자의 모양은 반응온도가 증가함에 따라 다각형의 모양이 얻어졌다. 225℃에서 8 시간 반응을 행한 경우의 평균입자 크기는 약 150 nm 이고, 입도분포는 균일하였다.

1. Introduction

The chemical, electrochemical, catalytic, and photocatalytic properties of zinc oxide can be utilized to advantage in many types of applications in batteries, fuel cells and photocells. Zinc oxide is a white pigment with high opacity to ultraviolet rays. Insoluble in water, solvents, and neutral oils, it possesses high brightness, fine particle size, and relatively high refractive index. The thermal properties of zinc oxide are useful in several major product categories, including rubber, ceramics, and electronics. Zinc oxides is amphoteric and, thus, is soluble in both acids and strong alkalies. In addition, it is soluble in solutions of ammonium salts. The many electronic properties of zinc oxide are utilized not only in the burgeoning photocopy market, but also in such diverse applications as i) catalysis, ii) magnetic ferrites, iii) phosphors, iv) photochemicals, v) piezoelectric materials, vi) semiconductors, and vii) varistors [1].

Recently, there has been an increasing interest in the synthesis of monodispered metal oxides. Solution synthesis techniques have the potential to meet the increasing demand for the direct preparation of crystalline ceramic powders and offer a low-temperature alternative to conventional powder synthesis techniques in the production of anhydrous oxide powders [2]. Solution synthesis techniques can produce fine, high-purity, stoichiometric particles of single and multicomponent metal oxides. Furthermore, if process conditions such as solute concentration, reaction temperature, reaction time and the type of solvent are carefully controlled, ceramic particles of the desired shape and size can be produced [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 [4]. 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 [5]. These powders could be sintered at low temperature without calcination and milling steps [6,7].

The concepts embodied in hydrothermal processing approaches can be extrapolated to nonaqueous systems. However, the reaction mechanisms in nonaqueous solutions are complex, and currently there is very limited information regarding the reaction thermodynamics, kinetics, and underlying crystallization mechanisms. Only a few investigations have dealt with the use of organic media to synthesize crystalline ceramic powders [8,9].

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 [10].

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

2. Experimental Procedure

The process for preparing ZnO by glycothermal treatment in 1,4-butanediol solution is schematically illustrated in Fig. 1. ZnO precursors were precipitated from 1 M $Zn(NO_3)_2 \cdot 6H_2O$ solution by slowly adding 1 M KOH solution with rapid stirring. The precipitated ZnO 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 250 ml 1,4-butanediol under vigorous stirring. The resulting suspension was placed in a 1000 ml stainless steel pressure vessel. 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 3.0 MPa during the holding period. After the treatment, the vessel was cooled to 25℃. The reaction products were washed at least five times by repeated cycles of centrifugation and redispersion in methanol. After washing, the recovered powders were dried at 100℃ in a dry oven 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).

3. Results and discussion

Homogeneous nucleation of zinc hydroxide occurred based on the nucleation and

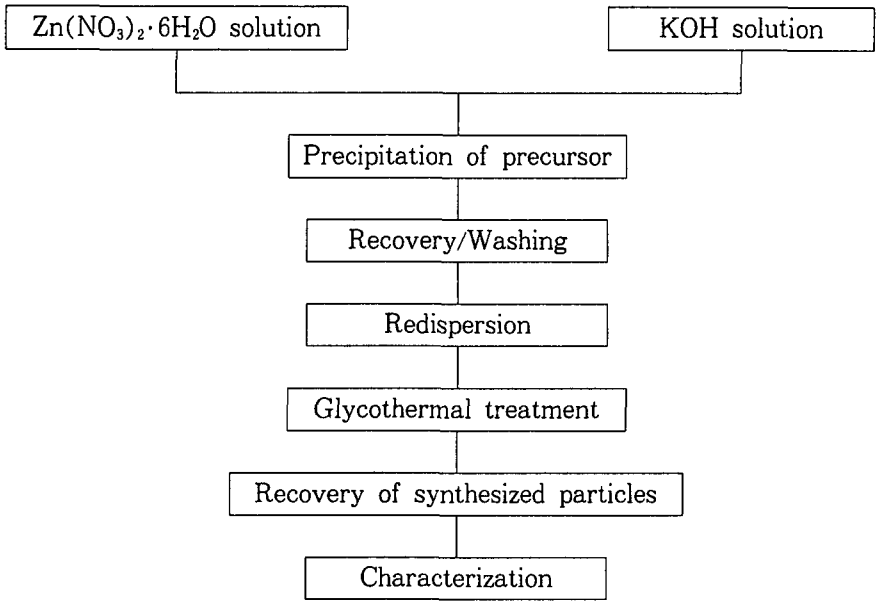

Fig. 1. Preparative procedure for the preparation of the ZnO particles in 1,4-butanediol solution.

Table 1
Synthesis conditions of the ZnO 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	5
2	250	10	no	5
3	270	10	no	5
4	300	5	no	5
5	270	10	30	5
6	270	10	no	2.5

growth process. A nucleation and growth process often determines the process temperature and process time. Their growth mechanism can be summarized as follows: (i) dissolution of the starting materials, (ii) transport of the Zn in the hydrothermal fluid, (iii) nucleation of the Zn oxide 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, the transport step, and the nucleationgrowth step.

Preparation of zinc oxide from metal permits considerable flexibility in control of particle size, particle shape and product

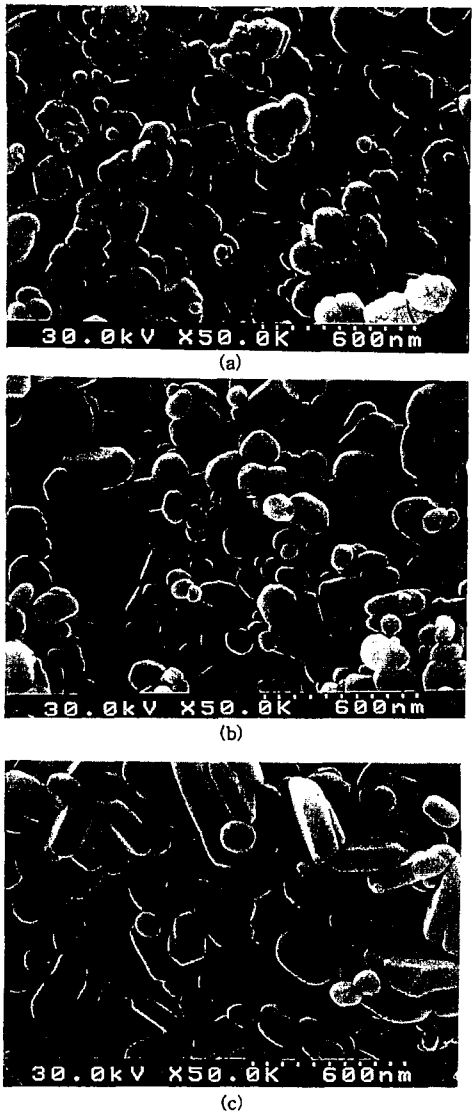

Fig. 2. SEM micrographs of the ZnO particles were synthesized by glycothermal treatment as a function of reaction temperature at (a) 225℃, (b) 250℃ and (c) 270℃.

purity. French process, average particle size may range from 0.1 μm to 10 μm. Particle size may range from fine to coarse and paricle shape from nodular to acicular [1].

Figure 2 shows the scanning electron micrographs of the synthesized ZnO powders. All the ZnO powders were synthesized at 225 to 275℃. Glycothermal synthesis of the ZnO from nitrates in KOH ied to somewhat nearly spherical and ultrafine particles which was on the order of 100 to 250 nm in size. The reaction temperature has an effect on the size and shape of the ZnO particles synthesized in 1,4-butanediol solution. 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 ZnO particles. The ZnO particles with higher reaction temperatures have larger polyhedron shape.

The sharp diffraction peaks consistant with the well defined and crystallized particles shown Fig. 3. The transformation of precursor to ZnO in 1,4-butanediol did occur in the range of 225 to 275℃ and 1 to 3.0 MPa, respectively.

Thus, the hydrothermal method used here led to ultrafine spherical particles which may be useful applications for various field.

4. Conclusions

Ultrafine, nearly spherical, and high purity of the zinc oxide was prepared by neu-

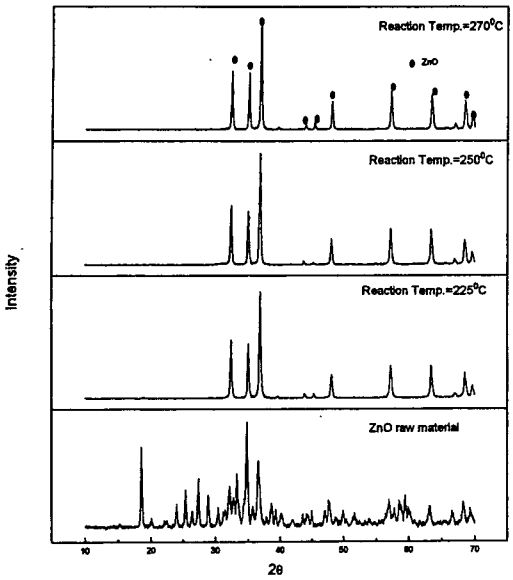

Fig. 3. X-ray diffraction pattern of the ZnO particles synthesized by glycothermal treatment (a) raw materials, (b) 225℃, (c) 250℃ and (d) 270℃.

tralizing the nitrate solutions in KOH under mild hydrothermal conditions.

After glycothermal treatment at 225℃ for 8 h, the average particle diameter of the ZnO was about 150 nm. The average particle size of the ZnO increased with increasing reaction temperature and time.

The shape of the synthesized ZnO powder became polyhedron and the distribution of average particle size became wide with increasing reaction temperature.

The results of this study show that it is possible to control the size of the ZnO particles in the range of about 100 to 300 nm glycothermally synthesized in 1,4-butanediol solution, if the synthesis conditions such as reaction temperatures and solid loading are carefully controlled.

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