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Preparation of spherical fine ZnO particles by the spray pyrolysis method using ultrasonic atomization techniques

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An ultrasonic atomizer was used in the spray pyrolysis method to prepare fine, spherical and uniform ZnO particles. Almost spherical particles were obtained successfully which had a mean particle size of 0.15 μm and had a very narrow particle size distribution. By using alcohol as the solvent, it was found that the particles do not have hollow shell layers which could usually be observed in the spray pyrolysis process by using water as the solvent. The morphology of the ZnO particles was strongly affected by the concentration of the starting solution.

1. Introduction

The electronic and structural ceramic components require good homogeneity both in composition and microstructure, high purity and high reliability. To be realized the ceramics having the above properties, fine-grained, aggregation-free and narrow size distribution powders are required. Of many chemical methods to prepare powders, the spray pyrolysis method seems to be one of the better methods to satisfy the requirements. The spray pyrolysis method was applied for many kinds of materials. Ruthner [1] successfully synthesized fine reactive ceramic powders (e.g. MgO, Al_2O_3, $MgAl_2O_4$). Roy *et al.* [2] prepared the fine powders of Al_2O_3 and $CaAl_2O_4$ in size of nearly 1 μm from metal nitrates. Gardner *et al.* [3] prepared oxides from many salts, such as nitrates, acetates, sulphates and chlorides, and also studied the characteristics of these powders and the effects of heating temperature. The properties (e.g. electrical, thermal property etc.) of iron oxide powder, β''-Al_2O_3, calcia stabilized zirconia and so on were examined by Kato *et al.* [4, 5, 6]. Since the usual nozzle atomizer process is not enough to control the size distribution of droplets and to decrease the particle size, we have tried to use the ultrasonic atomizer to prepare good droplets and obtain very fine, spherical and good size homogeneity powders of TiO_2 and $SrTiO_3$ by using metal alkoxides as the starting solution [7]. In the spray pyrolysis method, the most important technical points are the preparation of uniformly spherical and discrete droplets and the controlled thermal decomposition of these droplets. If the atomized mists were very fine and had a narrow size distribution in the spray pyrolysis method, uniform, fine and spherical powders can be prepared.

This paper describes the preparation of a spherical submicron ZnO powder with a narrow size distribution and the mechanism of powder formation by the ultrasonic atomizer driven spray pyrolysis method.

2. Experimental procedure

Fig. 1 shows the schematic diagram of apparatus for powder preparation. $Zn(CH_3COO)_2 \cdot 2H_2O$ as a starting material was dissolved in methyl alcohol. This solution was atomized into fine and uniform droplets using an ultrasonic atomizer. The droplets were carried into the low temperature furnace (No. 1 in Fig. 1) with a mixed gas of nitrogen and air, having the flow rate of 3.3 to 6.6 cm sec^{-1}. Considering the dehydration temperature and the decomposition temperature of the dihydrate zinc acetate is 100 and 240° C, respectively, the temperature of the low temperature furnace was set in 200° C.

Since methyl alcohol has a very high evaporation rate from droplets at a low temperature furnace, the droplets of alcohol solution changed into zinc acetate particles. The zinc acetate particles were then carried into the high temperature furnace which was kept about 500° C (No. 2 in Fig. 1) and changed into ZnO particles perfectly.

The ZnO powder was characterized by X-ray diffraction, thermal analysis and transmission electron microscopy.

3. Results and discussion

3.1. Particle morphology

Fig. 2 shows (a) SEM, (b, c) TEM and (d) electron diffraction patterns of the particles obtained from the concentration of 4.6×10^{-3} mol $litre^{-1}$. The particle size distribution calculated from TEM photographs was shown in Fig. 3. The geometric mean diameter

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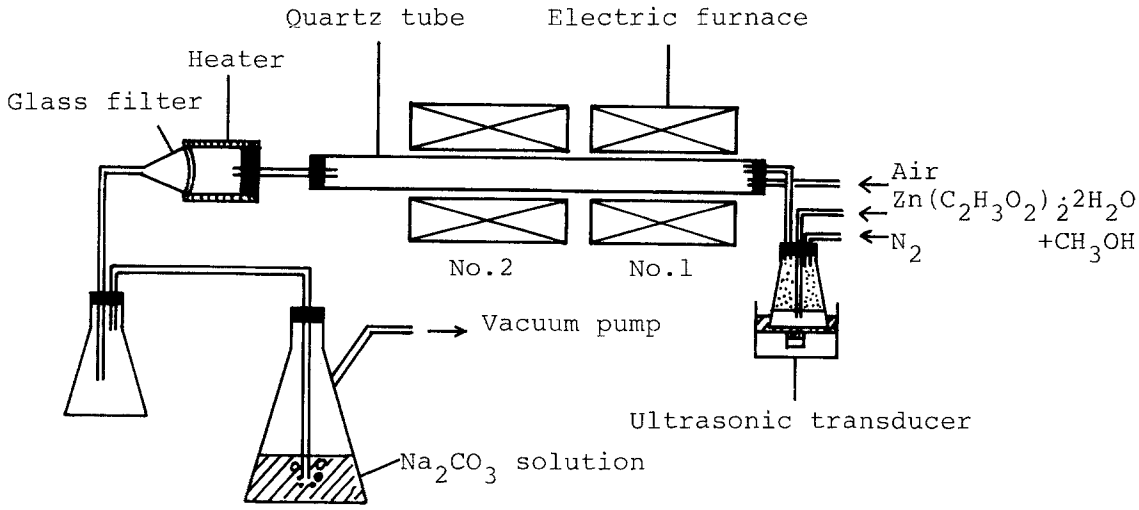

Figure 1 Schematic diagram of the experimental system.

and standard deviation were 0.15 μm and 1.50, respectively. The ultrasonic atomizer makes mists by vibrating the solution violently. The atomized mists have a very narrow size distribution and the mean size is determined by the equation [8]

$$d = 0.34\left(\frac{8\pi\gamma}{\varrho f^2}\right)^{1/3} \quad (1)$$

where γ is the surface tension of the solution, f is the frequency of the ultrasonic transducer and ϱ is the density of the solution.

Since the solution is very dilute, γ and ϱ can be assumed to be equal to the value of the pure methyl alcohol. If $\gamma = 22.5\,\mathrm{dyn\,cm^{-1}}$, $\varrho = 0.79\,\mathrm{g\,cm^{-3}}$ and $f = 1.7 \times 10^6\,\mathrm{Hz}$, droplet size is calculated $d = 2.14\,\mu$m from Equation 1. Assuming one ZnO dense particle is derived from one droplet, the mean diameter of dense ZnO particles can be calculated using the following equation:

$$d_{\mathrm{ZnO}} = \left(\frac{M_{\mathrm{ZnO}}}{M_{\mathrm{ZnAc}}}\frac{C}{\varrho_{\mathrm{ZnO}}}\right)^{1/3} d_{\mathrm{drop}} \quad (2)$$

where M_{ZnO} and M_{ZnAc} are the molecular weight of ZnO and zinc acetate, respectively. ϱ_{ZnO} is the density of ZnO and C is the concentration of the starting solution. d_{drop} is the mean diameter of the droplets. According to Equation 2, $d_{\mathrm{ZnO}} = 0.086\,\mu$m is obtained when assuming $C = 1 \times 10^{-3}\,\mathrm{g\,cm^{-3}}$, $\varrho_{\mathrm{ZnO}} = 5.67\,\mathrm{g\,cm^{-3}}$, $M_{\mathrm{ZnO}} = 81.4$, $M_{\mathrm{ZA}} = 219.5$ and $d_{\mathrm{drop}} = 2.14\,\mu$m.

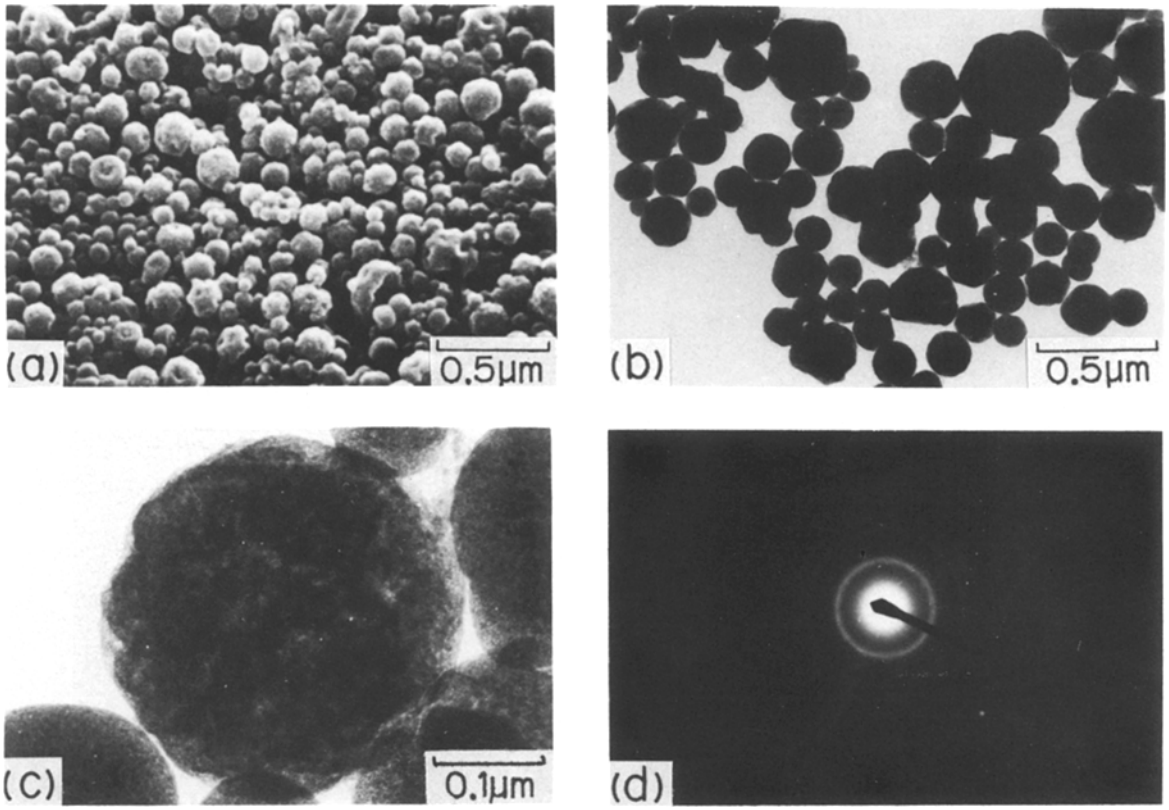

Figure 2 Electron micrographs of ZnO powder prepared at $C = 4.6 \times 10^{-3}\,\mathrm{mol\,litre^{-1}}$.

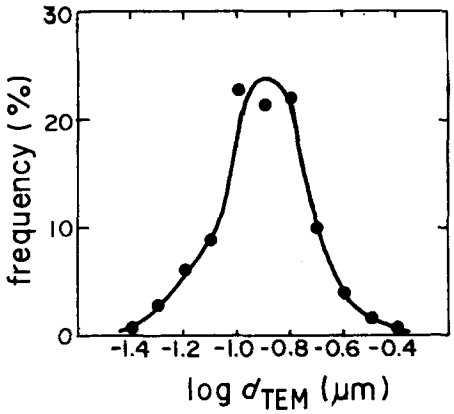

Figure 3 Particle size distribution of ZnO powder. T_2 = 500° C; $C = 4.6 \times 10^{-3}$ mol litre^{-1}; V = 1.8 litre min^{-1}.

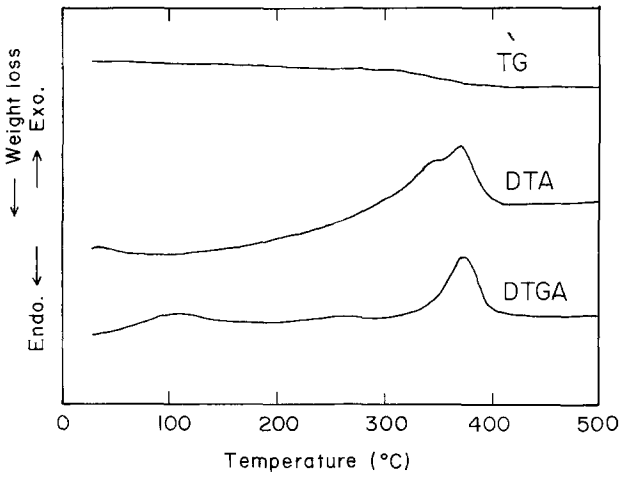

Figure 5 Thermal analysis of as-prepared ZnO powder.

Particle size (d_{ZnO}) calculated from Equation 2 is smaller than the mean ZnO diameter measured by TEM photographs. This suggests that the obtained particles are not perfectly dense but slightly porous. From Fig. 2, further, one spherical particle is composed of individual particles that are between 100 and 200 nm in diameter and its surface area is about 50 m^2 g^{-1} corresponding to 200 nm. This evidence suggests that one spherical ZnO particle is slightly porous and composed of individual smaller particles or so-called "primary particles" in diameter of 200 nm. But the ZnO particle has not such hollow structure as observed usually in particles made by the spray pyrolysis method using water as a solvent. This difference in microstructure is due to a very rapid evaporation of methyl alcohol which gives no time to form a spherical shell layer on particle surface during evaporation.

The TEM photograph of reheated particles to 500° C is shown in Fig. 4. The primary particles take very clear shape of about 200 nm in diameter and seem to have very good crystallinity from the diffraction patterns. By this evidence, it can be suggested that the primary particles exist also in as-prepared particles, but because of their poor crystallinity (Fig. 2d), they cannot be distinguished easily from TEM observation. However, in heating the powder the crystallization proceeds and finally the primary polycrystal particles grow into almost single crystal and take a very clear shape.

Fig. 5 shows the DTA–TG and DTGA curves of as-prepared ZnO powder. The weight loss of about 5% is observed due to evaporation of water absorbed in the particles and decomposition of the unreacted organic substance, corresponding to the peaks of DTA and DTGA curve in 100 and 370° C, respectively. The exothermic DTA peak from 200 to 400° C must be due to the crystallization of ZnO and the decomposition of residual organic materials.

3.2. Particle characteristics

The shape and microstructure of particles are extremely affected by the reaction conditions, particularly by the concentration of zinc acetate in solution. Fig. 6 shows various ZnO particles prepared from different concentration. In higher concentration of zinc acetate, a lot of new-type ultra-fine particles of 0.01 μm (diameter) co-prepared with the large spherical particles similar to those shown in Fig. 2 and always co-exist in the case of $C > 4.6 \times 10^{-3}$ mol litre^{-1}. And the higher the concentration of zinc acetate, the more the ultra-fine particles.

Fig. 7 shows the relation between the particle size and the concentration, where lines (a) and (b) give the particle size measured for the spherical particles

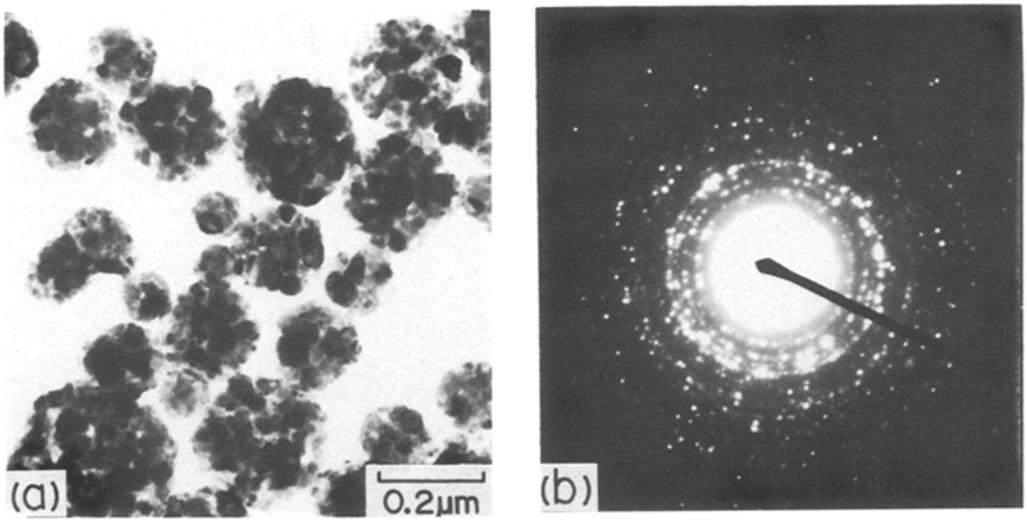

Figure 4 Electron micrographs of ZnO powder after heat treatment.

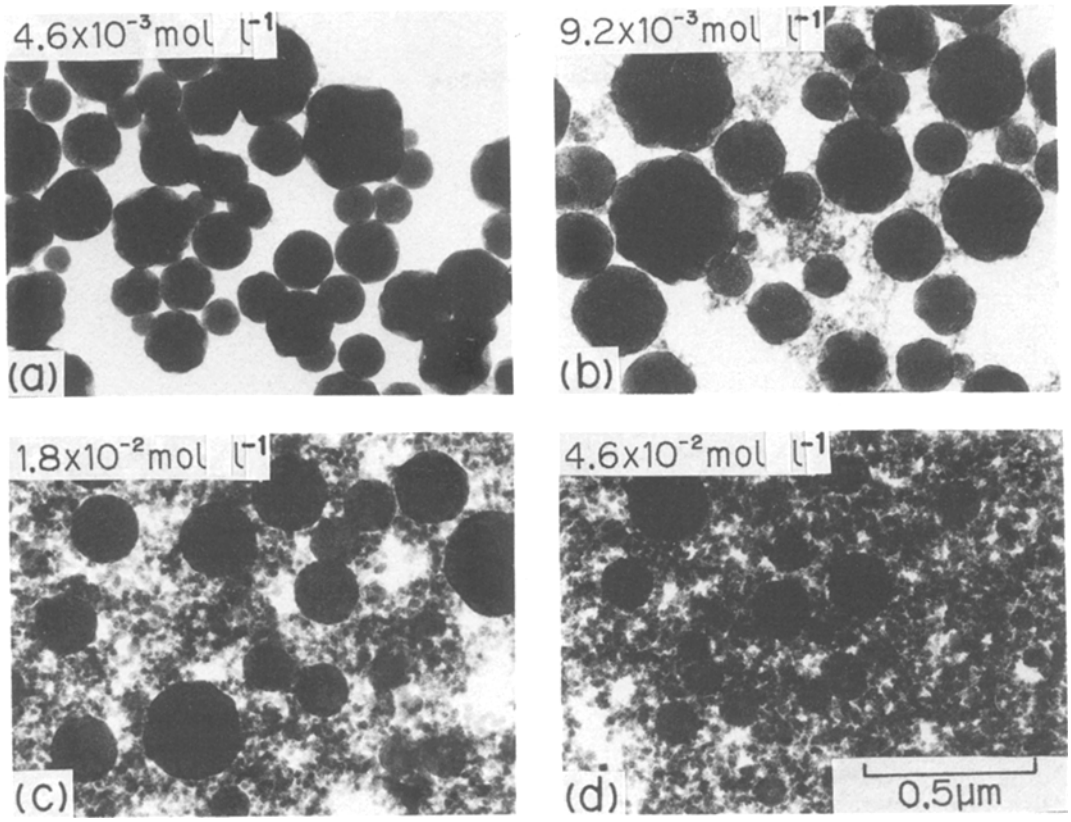

Figure 6 TEM of ZnO powder prepared at different concentrations.

shown in Fig. 6 (but no counting for the ultra-fine particles), and calculated from Equation 2, respectively. Assuming that one particle is derived from one droplet and the droplet size is constant as independent on the concentration, the ZnO particle size should increase with the concentration as shown in Fig. 7 (line (b)). However, the measured particle size increases with the concentration only in the range of low concentration and subsequently the increase of the concentration decreases the particle size in contrast to prediction. Above unusual phenomena can be understood following Fig. 8.

$Zn(CH_3COO)_2$ has a melting point of about 240° C and considerably high vapour pressure around 200° C. According to our preliminary experimental results, the weight loss of 5 to 10% was observed by heating the anhydrous zinc acetate at 200° C for 1 h. If the anhydrous zinc acetate particles after dehydration are exposed to a hot atmosphere such as in a low temperature furnace, zinc acetate vaporizes from the surface of the particles. Even if the particles stay in the furnace for very short time, the particles become very small, i.e. the surface is very large, so the total evaporation rate can be suggested to be very large. This evaporation becomes rapid and vigorous with increasing zinc acetate concentration because the droplets with higher concentration tend to lose the alcohol as solvent more quickly and form zinc acetate particles more easily.

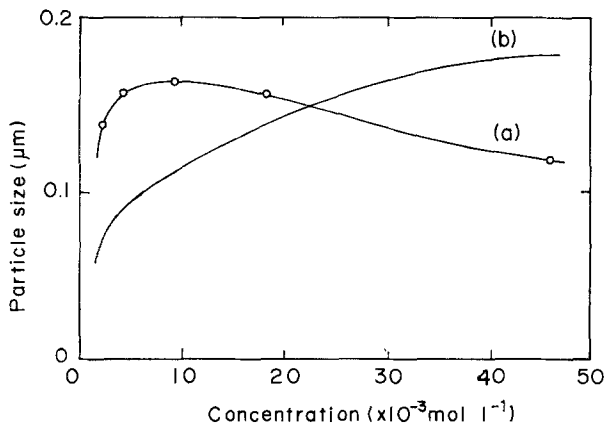

Figure 7 Change of the mean particle size with concentration. T = 500° C; V = 1.8 litre min^{-1}.

As shown in Fig. 8, in the case of high concentration, around the outlet of the low temperature furnace (No. 1), both of the vapour and the solid particles of zinc acetate are considered to be present. The vapour will then be pyrolysed to the ultra-fine particles in the high temperature furnace (No. 2).

We can also consider the effects of flow rate. In practice, the higher the flow rate the less the ultra-fine particles, and the larger the mean particle size of large ZnO particles. That is, the higher the flow rate, the shorter the evaporating time, so the less the amount of vapour, and the larger the particle size.

4. Conclusions

The spray pyrolysis method with an ultrasonic atomizer gave spherical, aggregation-free, uniform size of 0.15 μm particles. The ZnO particle was composed of many primary particles of 100 to 200 nm in diameter, and had very large surface area about 50 $m^2 g^{-1}$.

The particle characteristics are affected by the concentration of solution and the flow rate of carrier gas, substantially. When the concentration increased, ultra-fine particles in diameter of nearly 100 to 200 nm

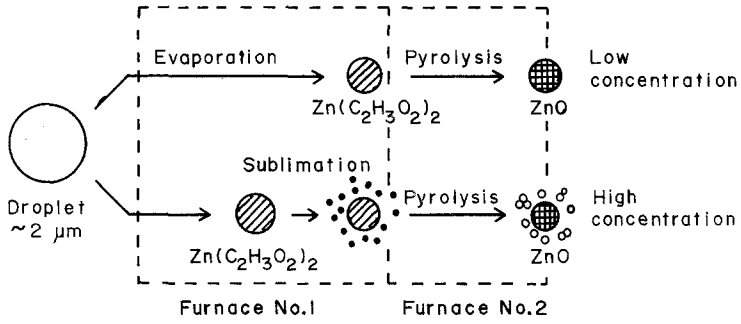

Figure 8 Schematic representation of formation mechanism for ZnO particles.

appeared, accompanied with the ZnO particles. The higher the concentration increases, the more the ultra-fine particles appear, and the lower the flow rate becomes, the larger the ultra-fine particles can be obtained.

It can be concluded that the high vapour pressure of zinc acetate is responsible for the occurrence of the ultra-fine particles. This evaporation–pyrolysis process of zinc acetate gives promising processes for the production of ultra-fine oxide uniform particles.

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