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Preparation of Monodisperse ZrO_2 by the Microwave Heating of Zirconyl Chloride Solutions

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Based on the principle that the solubility of a salt decreases as the dielectric constant of the solvent decreases, zirconia powders were prepared by heating a zirconyl chloride solution with a 2-PrOH–water mixture as the solvent. The morphology, size, and size distribution of the resulting particles were highly sensitive to the heating method used on the starting solution. Particles formed under conventional heating methods were polydisperse, agglomerated spherical, or irregularly shaped because of inhomogeneous precipitation through the temperature gradient, the shear force induced by stirring, compositional nonuniformity, and the low heating rate. The present study demonstrated that microwaves provide an excellent means of heating uniformly and rapidly without stirring. The particles resulting from microwave treatment were monodisperse and spherical, with a mean diameter of 0.28 μm.

I. Introduction

RECENT investigation has suggested that monodisperse spherical powders are preferable to others for enhancing densification and grain growth in ceramics. Several novel methods using wet chemistry have been developed for the preparation of powders with spherical shape and uniform size. Numerous studies, however, have shown that experimental conditions such as stirring speed, temperature uniformity, and pH uniformity in the reactor are crucial parameters for determining the shape, size, size distribution, and dispersity of the particles. Look and Zukoski[1] demonstrated that titania-precipitate morphologies were quite sensitive to the level of agitation in the reactor. Williams *et al.*[2] reported that spherical, monodisperse zinc sulfide particles could be obtained by a homogeneous precipitation reaction using thioacetamide. These researchers pointed out that monodisperse and spherical powders did not form under vigorous stirring of the reaction mixture or with an existing temperature gradient in the reaction vessel. In emulsion polymerization,[3] shear-induced aggregation was recognized as a major deterrent to controlling the final particle size distribution in the large reactor.

According to a report by Hasted,[4] the dielectric constant of an alcohol–water mixed solvent decreases with increases in the volume ratio of alcohol to water and/or temperature. The solubility of an inorganic salt decreases with decreases in the dielectric constant of the solvent.[5,6] In separate experiments it was demonstrated that a spherical zirconia powder can be synthesized by controlling the dielectric constant of the solvent mixture. This method, however, is influenced significantly by such experimental conditions as stirring speed, temperature uniformity, and heating rate.

Microwaves are widely used in today's materials processing technology. Microwave heating provides the following properties:[7] (1) volumetric heating rather than the surface absorption and thermal diffusion afforded by conventional heating, (2) potentially "uniform" heat distribution, (3) rapid heating rates, and (4) the possibility of selectively heating desired materials. To date, the most common applications of microwave technology in ceramic processing include binder removal,[8] drying,[9] joining,[10] and sintering.[11,12] Recently, several research groups have reported that microwave processing holds promise for the synthesis of chemical compounds and materials.[9,13–15]

The present work enumerates the problems induced when a zirconia powder is precipitated by conventional methods from a zirconyl chloride solution with a 2-PrOH–water mixture as the solvent. Microwave heating then is demonstrated to offer a new method for solving these problems.

II. Experimental Procedure

The starting material in the present study was zirconyl chloride octahydrate (98% $ZrOCl_2 \cdot 8H_2O$, Aldrich Chemical, Milwaukee, WI). Doubly distilled water and GR-grade 2-propanol were used for preparing the alcohol–water mixture. Hydroxypropyl cellulose (HPC) (molecular weight ~100 000, Nakalai Tesque, Japan) was used as a dispersant. The concentration of zirconyl chloride was 0.2*M*, and the volume ratio of 2-PrOH to water in the starting solution was 5. The volume of the starting solution was 60 mL in all experiments. The HPC concentration was 1.0×10^{-3} g/cm^3, based on the total solution volume. All reagents and solvents were used in the as-received form, with no further purification.

When the solution was heated, it became supersaturated and precipitated at ~26°C. Precipitation was continuous up to approximately the boiling temperature of the starting solution. The influences of experimental conditions such as stirring rate, temperature uniformity, and heating rate on the powder characteristics were observed by serial experimentation, as shown in Table I. First, the effect of shear force and temperature gradient on the precipitate morphology was observed by rapidly heating the solution through abrupt immersion of the reaction vessel into a thermostatted bath with and without stirring. The temperature of the bath was maintained at 80.3°C, the boiling temperature of the 2-PrOH–water mixture with a 2-PrOH-to-water volume ratio of 5.[16] Next, the reaction vessel was heated in a water bath with and without stirring to reveal the effects of the precipitation-reaction rate and the sedimentation rate on the precipitate morphology. The temperature of the water bath was increased to 80.3°C slowly, at a rate of 0.3°C/min, to minimize the temperature gradient in the reaction vessel. Then, to demonstrate the effects of the concentration gradient on the precipitate morphology, precipitation was initiated by abruptly mixing the zirconyl chloride aqueous solution with the 2-PrOH at 80.3°C. Finally, problems caused by conventional heating methods were eliminated by using microwave heating to produce the precipitation reaction. The heating apparatus was an ordinary kitchen microwave oven (2.45 GHz, 650 W).

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Table I. Morphology, Mean Size, and Size Distribution of Particles Obtained by Various Heating Methods

Heating method	Heating rate (°C/min)	Stirring rate (rpm)	Temperature uniformity	Mean particle size (μm)	σ_g*	Particle morphology
Abrupt immersion to the thermostat bath of 80.3°C	15	0	Nonuniform	0.29	1.25	Spherical, polydispersed
	15	600	Uniform	0.36	1.20	Spherical, agglomerated
Slow heating to 80.3°C by heating of the bath	0.3	0	Uniform			Irregular, agglomerated
	0.3	600	Uniform	0.43	1.29	Spherical, polydispersed
Abrupt mixing of 2-PrOH and aqueous salt solution of 80°C		600	Uniform but presence of vigorous concentration gradient			Irregular, agglomerated
Microwave heating	120	0	Uniform	0.28	1.12	Spherical, monodispersed

*Geometrical standard deviation of particle size.

The precipitate resolved reversibly into the mother liquor during cooling because of the increased dielectric constant of the medium. This problem was solved by adding a 4*N* NH_4OH solution, which neutralized the mother liquor. The precipitates were centrifuged repeatedly (at 10 000 rpm for 5-min intervals) and washed in distilled water until no chloride ions could be detected in the supernatant solution. The water-washed precipitates then were dried for 6 h in a vacuum oven at 60°C. The morphology, size, and size distribution of the resulting particles were investigated by scanning electron microscopy (SEM).

III. Results and Discussion

The effects of heating method on the morphology, size, and size distribution of the resulting particles are summarized in Table I.

(1) Stirring Effect

Figure 1(a) shows particles obtained when the solution was heated rapidly by abrupt immersion of the flask into a thermostatted bath at 80.3°C with no stirring. The particles were spherical but with a broad size distribution; the particle size and its geometric standard deviation (σ_g) were 0.29 μm and 1.25, respectively. Homogeneous precipitation could not occur because local supersaturation took place from the vessel wall, which was preferentially heated. Generally, the temperature gradient under a conventional heating method may increase as the size of the reaction vessel and the heating rate increase. Actually, in the present study, the particle size distribution was more broad when the solution was heated on a hot plate or a heating mantle than when the immersion method was used.

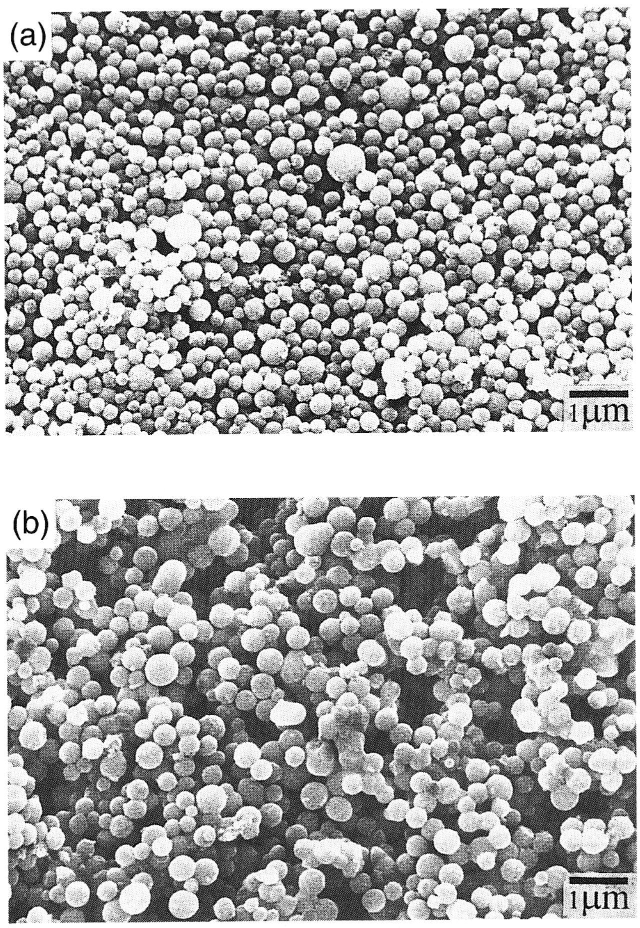

Fig. 1. SEM micrographs of the particles obtained when the solution was rapidly heated by abrupt immersion of flask into thermostat bath of 80.3°C (a) without and (b) with stirring.

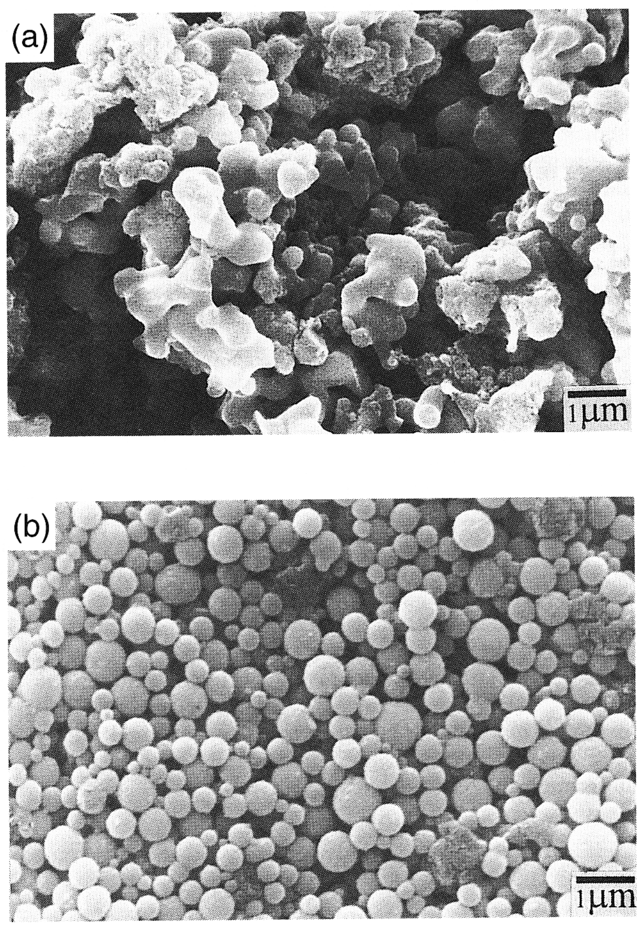

Fig. 2. SEM micrographs of the particles obtained when the solution in a flask was deeply immersed in a water bath and slowly heated to 80.3°C with 0.3°C/min, (a) in the absence of stirring and (b) in the presence of stirring.

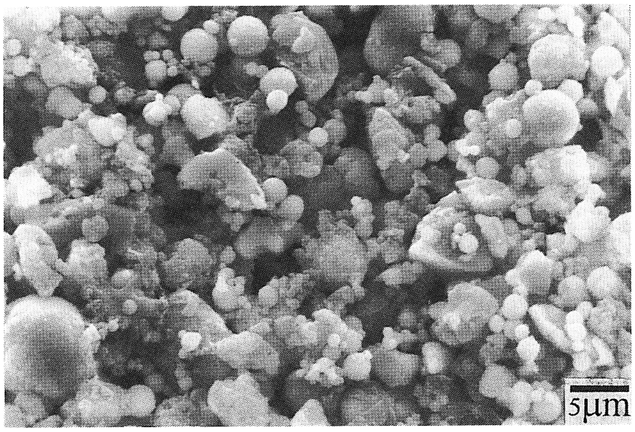

Fig. 3. SEM micrographs of the particles obtained from abrupt mixing of zirconyl chloride aqueous solution and 2-propanol solvent containing HPC which were preheated to 80.3°C.

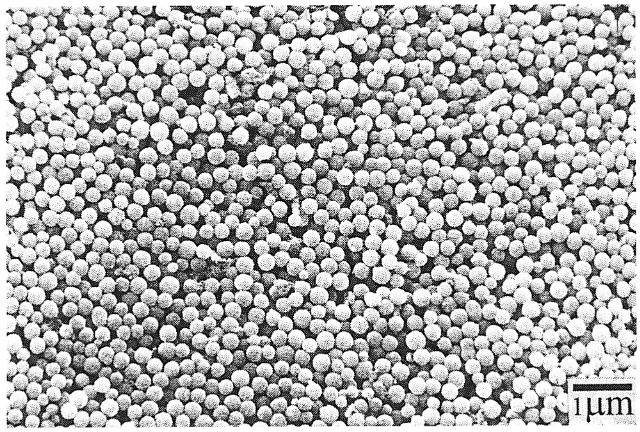

Fig. 4. SEM micrographs of the particles obtained when the solution was very rapidly heated to 80.3°C by microwave without stirring. Heating rate was 120°C/min.

To remove or minimize the temperature gradient of the solution within the reaction vessel, the solution was stirred vigorously during the reaction. Figure 1(b) shows the particles obtained from this method. These particles were spherical, with a narrow size distribution, but they were highly agglomerated and had a large mean diameter; the particle size and its geometric standard deviation (σ_g) were 0.36 μm and 1.20, respectively. Thus, the particle size distribution can be decreased somewhat by stirring, which minimizes the temperature gradient of the solution, but vigorous stirring can cause shear-induced aggregation.[1–3] The resulting particles will consist of agglomerated masses fused together by the shear force. The particle size becomes larger than that formed with no stirring because the collision frequency of the particles is increased by stirring.[17] The present results demonstrated that a new heating method, which can improve temperature uniformity without stirring, is necessary for the creation of monodisperse and unagglomerated particles.

(2) *Heating Rate Effect*

Figure 2 shows the morphology of the particles obtained in a reaction vessel deeply immersed in a water bath whose temperature was increased to 80.3°C slowly (at the rate of 0.3°C/min) to avoid the temperature gradient. The morphology of the particles was very sensitive to stirring. In the absence of stirring, a large amount of precipitates settled to the bottom of the reaction vessel before the precipitation reaction was complete. Accordingly, subsequent precipitation resulted mainly in the growth of a neck between these particles. In contrast, with stirring the majority of particles stayed in suspension during the entire precipitation reaction and grew in a more symmetrical environment.

The degree of agglomeration induced by the shear force was higher at a high heating rate than at a low rate, as shown by Figs. 1(b) and 2(b). Apparently, the relief rate of supersaturation at the nucleation stage increased with the increased heating rate. Such a phenomenon means that the number of primary and secondary particles formed at the initial precipitation stage increased, and a relatively small amount of species remained in solution. The degree of agglomeration therefore increased at a high heating rate because the collision frequency induced by stirring increased. These results correspond to those of Look and Zukoski,[1] in whose study the critical shear rate was found to decrease sharply as the concentration of the solute in the reacting solution was raised. Under a low heating rate, the secondary particles grew continuously by aggregation of the primary particles, and the molecular addition of the species remained in solution during heating. The particles obtained under a low heating rate therefore became larger than those obtained under a high rate. It thus appears necessary to find a new method for heating the solution rapidly and uniformly to achieve monodisperse and unagglomerated particles.

(3) *Mixing Method*

Figure 3 shows particles obtained by abruptly mixing the zirconyl chloride aqueous solution and the 2-PrOH preheated at 80.3°C. These particles consisted of large and small spheres and, in most cases, irregularly shaped agglomerates. Inhomogeneous precipitation therefore occurred because of the concentration gradients of the solute and the solvent. Recently, Li and Messing[17] and Mizutani[6] reported that the dielectric constant of the solvent mixture greatly influences the precipitation behavior of a salt solution and the morphology of the resulting particles. Supersaturation is quite high locally in the 2-PrOH-rich region when 2-PrOH is added abruptly, because the dielectric constant of the solvent decreases rapidly. This fluctuation of supersaturation throughout the solution may inhibit homogeneous precipitation. Such a phenomenon is similar to the pH shock caused by the usual precipitation methods, in which precipitation is accomplished by the addition of precipitating agents such as NH_4OH. It therefore is difficult to synthesize monodisperse spherical particles by mechanical mixing of the solvents.

(4) *Microwave Heating*

To produce nonagglomerated spherical particles of uniform size, a heating method must satisfy several conditions, such as minimizing the stirring speed, temperature gradient, and concentration gradient and maximizing the heating rate. In the present work, rapid and uniform heating of the starting solution was achieved without stirring by using a microwave source. Figure 4 shows the particles obtained by microwave heating. These particles were spherical, with diameters of 0.28 μm and a geometric standard deviation (σ_g) of 1.12 (Fig. 5).

The basic interaction mechanisms between a microwave source and a material depend strongly on the dielectric and

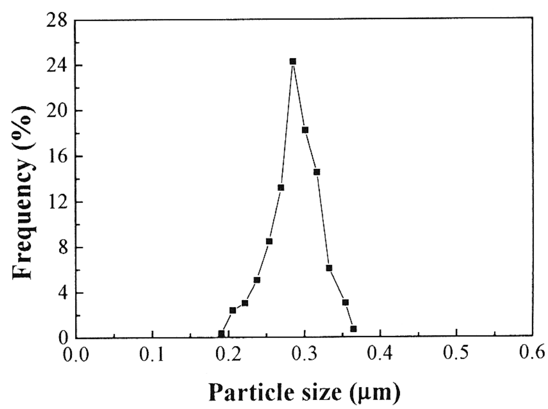

Fig. 5. Particle size distribution of the particles obtained by microwave processing.

magnetic properties of the processed material. Because a starting solution with a high loss factor absorbs microwaves very well, and the Pyrex flask used as a reaction vessel in the present work was microwave-transparent, the starting solution was uniformly heated by microwaves; the heat was not conducted into the starting solution from outside. No shear-induced aggregation took place, because stirring could be eliminated with microwave heating. Furthermore, heterogeneous nucleation at the container wall was suppressed, and precipitation occurred simultaneously throughout the solution. Such results indicate that several problems posed by conventional heating methods can be solved effectively through microwave heating.

IV. Conclusions

Monodisperse, spherical zirconia powders can be prepared by the microwave heating of a zirconyl chloride solution with a 2-PrOH–water mixture as the solvent. This unique method may eliminate many problems, such as the temperature gradient, low heating rate, compositional nonuniformity, and shear force induced by vigorous stirring, that are inevitable under conventional heating methods.

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