

# Processing and Characterization of ZrO<sub>2</sub> and Y-Doped ZrO<sub>2</sub> Powders

BRUCE FEGLEY, Jr.,\* PAUL WHITE,\* and H. KENT BOWEN\*

Massachusetts Institute of Technology, Cambridge, MA 02139

Historically, a great deal of effort was spent on the synthesis of small-particle-size ceramic powders.<sup>1-3</sup> The apparent desirability of these powders, which may be  $\leq 1.0 \mu\text{m}$  in size, was based on the greatly enhanced sintering kinetics which were predicted for fine powders.<sup>4</sup> However, the expected advantages of shorter sintering times and lower sintering temperatures were generally not achieved unless special efforts were made to eliminate agglomerates and to control the initial particle size distribution.<sup>3,5</sup> The importance of controlling the agglomeration and particle size distribution of fine powders is now generally acknowledged (e.g. as indicated by the large number of papers on this subject in a recent book on ceramic processing).<sup>6</sup>

One method for controlling important powder characteristics such as size, shape, size distribution, and state of agglomeration is the *controlled* hydrolysis of metal alkoxides.<sup>7-10</sup> These reactions have several advantages which make them an attractive route for producing ceramic powders. The utility of alkoxide decomposition reactions for producing high purity oxide powders with small particle size is well known.<sup>1</sup> Furthermore, controlled alkoxide hydrolysis reactions are rapid (seconds to minutes), involve fairly simple solution chemistry, give a high chemical yield, can be done at fairly high alkoxide concentrations ( $\approx 1M$ ), and are easily adaptable to continuous processing schemes.<sup>8-11</sup>

Barringer and Bowen<sup>8</sup> recently demonstrated that the controlled hydrolysis of titanium alkoxides gave monodisperse TiO<sub>2</sub> powders which could be sintered to 99+% of theoretical density at temperatures several hundred degrees lower than those required to sinter conventional TiO<sub>2</sub> powders. Their success parallels Rhodes'

Monodisperse spheroidal zirconia and yttria-stabilized zirconia particles with an average diameter of  $\approx 0.2 \mu\text{m}$  were prepared by the controlled hydrolysis of zirconium and yttrium alkoxides. The particles can be formed into uniformly packed green pieces which sinter to uniformly sized fine-grained ceramics with >98% of theoretical density at temperatures as low as 1160°C.

success in sintering specially prepared yttria-stabilized zirconia (YSZ) powders at temperatures several hundred degrees lower than agglomerated zirconia powders.<sup>5</sup> These two demonstrations and Mazdiyasi's work<sup>1</sup> on zirconia synthesis by alkoxide decomposition led one of us (B.F.) to start a series of experiments on the preparation of monodisperse zirconia and YSZ powders. These powders were prepared by the controlled hydrolysis of zirconium and yttrium alkoxides.

This report describes the preparation, characterization, processing, and sintering of monodisperse zirconia and YSZ powders. The results demonstrate that these powders can be sintered to high density, fine-grained zirconia ceramics at temperatures as low as 1160°C. Furthermore, the small size, narrow size distribution, spheroidal shape, high chemical purity, and ease of preparation of these powders also makes them desirable starting materials for the fabrication of zirconia-bearing ceramics.

## Experimental Procedure

### Preparation of Monodisperse Powders

A large number of experiments were done on the synthesis of monodisperse zirconia by the controlled hydrolysis of zirconium *n*-propoxide\* and isopropoxide.\* Typical reaction parameters are listed in Table I. The basic procedure was described by Fegley and Barringer<sup>10</sup> and is not repeated here. However we want to emphasize several points. The controlled hydrolysis reactions must be done in a water-free atmosphere (e.g. in a glove box) using anhydrous alcohols and alkoxides and deionized water. Any small amounts of water in the atmosphere, alcohols, or alkoxides will

\*Member, the American Ceramic Society.  
\*Alfa Products, Danvers, MA.

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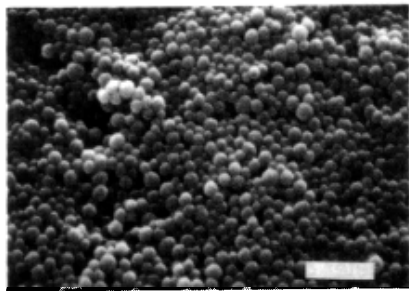


Fig. 1. Scanning electron micrograph of undoped zirconia made by controlled hydrolysis of zirconium *n*-propoxide in January 1983 (bar=1  $\mu\text{m}$ ).

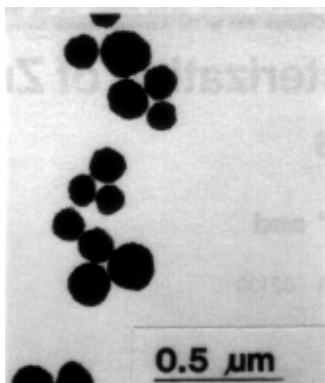


Fig. 2. Transmission electron micrograph of undoped zirconia (*n*-propoxide derived, water-washed).

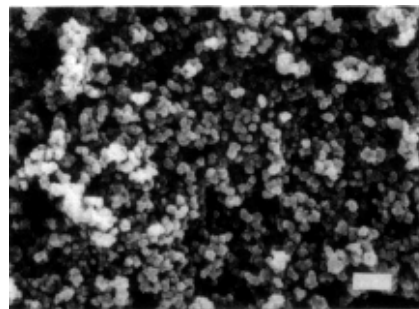


Fig. 3. Scanning electron micrograph of undoped zirconia made from zirconium isopropoxide in July 1983 (bar=1  $\mu\text{m}$ ).

cause uncontrolled hydrolysis reactions. Also as Table I illustrates, the precipitation times depend upon the reaction temperature. For example, experiments with zirconium *n*-propoxide show that 50°C is a good reaction temperature for producing small, monodisperse particles in a short time. Also, use of the zirconium *n*-propoxide-alcohol adduct supplied commercially\* gave the best powders. Distilled zirconium *n*-propoxide did not give monodisperse powders; agglomerated gel-like powders resulted instead (C. Sobon and P. White, unpublished data). Finally, the order of addition of the reactants is reversible and does not affect the morphology of the resulting powders.

YSZ powders were prepared by the controlled hydrolysis of a solution of yttrium and zirconium propoxides. Mazdiyasi et al.<sup>12</sup> first prepared YSZ powders by alkoxide hydrolysis. Our work differs from theirs because monodisperse particles of controlled size, shape, and size distribution were produced in our experiments. The solid yttrium isopropoxide used in the initial experiments was synthesized by Dr. H. Okamura using Mazdiyasi's procedures.<sup>13-14</sup> Later experiments were done with commercial yttrium isopropoxide.\* Dr. Okamura also prepared several batches of YSZ powders. These experiments were done using dry isopropanol as a solvent and the powders were strongly agglomerated. Subsequent experiments utilized anhydrous ethanol as a solvent. The second procedure, which was also described by Fegley and Barringer,<sup>10</sup> gave more spheroidal and less agglomerated powders. (The same considerations described for the undoped zirconia precipitation reactions also apply to the YSZ reactions.)

After precipitation the powders were washed by centrifuging and ultrasonically<sup>†</sup> redispersing in deionized water or ethanol. The washing cycle was repeated two to three times. Suspensions were prepared by ultrasonically dispersing the wet powders in water. After adjusting the pH to ten the dispersion was poured into a plastic vial (with a removable bottom) and allowed to settle for several days. Then the supernatant liquid was drawn off and the compact was air dried at room temperature.

#### Characterization Techniques

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) were used to estimate particle size and morphology. Quantitative size distributions were measured by dynamic laser light scattering (photon correlation spectroscopy) using the Coulter Model N4D.<sup>‡</sup> Specific surface areas of the powders were measured by N<sub>2</sub> gas adsorption (multi-point BET method.)<sup>§</sup> Powder densities were measured by a stereopycnometer<sup>||</sup> using He gas. Crystallinity was determined by powder X-ray diffraction using CuK $\alpha$  radiation. Differential thermal analysis (DTA)\*\* and thermogravimetric analysis (TG)\*\* were done in air at a heating rate of 10°C/min. Chemical analyses on powders were done by inductively coupled plasma spectroscopy (ICP).<sup>15</sup> Ceramics were analyzed by wet chemistry, proton induced X-ray emission (PIXE),<sup>††</sup> and electron probe microanalysis (EPMA).<sup>‡‡</sup> The EPMA data were taken at 15 kV and 30 nA; well characterized standards at the Department of Geological Sciences, Harvard University, were used in the analyses.

#### Results and Discussion

##### Particle Size, Shape, Size Distribution, and State of Agglomeration

SEM demonstrated that the pure zirconia powders made by the controlled hydrolysis of zirconium *n*-propoxide were composed of spheroidal, narrowly sized, unagglomerated particles of  $\approx 0.2 \mu\text{m}$  diameter. These desirable powder characteristics have been maintained in over 50 separate batches of powder made by several people over a 2-yr period. This is illustrated by comparing Fig. 1, which is a SEM micrograph of pure zirconia synthesized in January 1983, with Figs. 4(A) and 4(B) of Fegley and Barringer,<sup>10</sup> which are SEM micrographs of pure zirconia synthesized in July 1983. (Note: Figures 4(A),(B) and 5(A),(B) in Fegley and Barringer<sup>10</sup> are matched with the wrong captions.)

TEM micrographs also illustrate the desirable characteristics of the *n*-propoxide derived zirconia. Figure 2 is a TEM micrograph

Table I. Typical Reaction Conditions for Preparation of Monodisperse Powders

| Parameter                  | Zirconia powders    |              | Yttria-stabilized zirconia   |
|----------------------------|---------------------|--------------|--|
|                            | I                   | II           |  |
| Precursor(s)               | <i>n</i> -Propoxide | Isopropoxide | Y(OC <sub>3</sub> H <sub>7</sub> ) <sub>3</sub> and Zr(OC <sub>3</sub> H <sub>7</sub> ) <sub>4</sub> |
| Alkoxide concentration (M) | 0.1                 | 0.1          | 0.08 (Zr)<br>0.01 (Y)  |
| Water concentration (M)    | 0.5                 | 0.92         | 1.0  |
| T (°C)                     | 50                  | 25           | 50   |
| Precipitation time (s)     | 120                 | 11           | 120  |
| Typical yield (%)          | $\approx 60$        | $\approx 95$ | $\approx 60^*$   |

\*Yield of 45% given in Ref. 10 represents hydrolysis in dry isopropanol done by Dr. H. Okamura.

<sup>†</sup>Model W-220, Heat Systems-Ultrasonics, Inc., Farmingdale, N.Y.

<sup>‡</sup>Coulter Electronics, Inc. Hialeah, FL.

<sup>§</sup>Quantasorb, Quantachrome Corp., Syosset, NY.

<sup>||</sup>Quantachrome Corp., Syosset, NY.

<sup>\*\*</sup>Netzsch Corp., Exton, PA.

<sup>††</sup>Element Analysis Corp., Tallahassee, FL.

<sup>‡‡</sup>Cameca MBX, Cameca Corp., Los Angeles, CA.

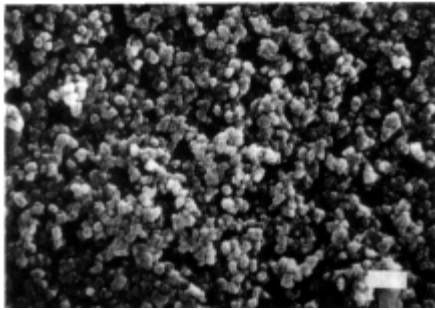


Fig. 4. Scanning electron micrograph of yttria-stabilized zirconia powder made by hydrolysis in isopropanol (bar=1  $\mu\text{m}$ ).

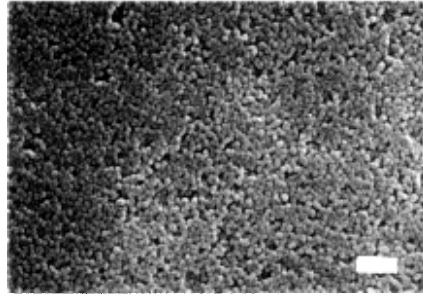


Fig. 5. Scanning electron micrograph of yttria-stabilized zirconia made by hydrolysis in ethanol (top surface of gravity-sedimented compact) (bar=1  $\mu\text{m}$ ).

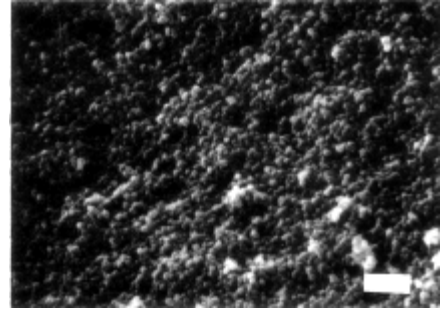


Fig. 6. Scanning electron micrograph of fracture surface of yttria-stabilized zirconia compact shown in Fig. 5 (bar=1  $\mu\text{m}$ ).

of zirconia made in August 1984 and Fig. 1(B) of Fegley and Barringer<sup>10</sup> is a TEM micrograph of zirconia made in February 1984. Again, the reproducibility of the zirconia powders made months apart is demonstrated.

By contrast, the isopropoxide derived zirconia (see Fig. 3) possesses less desirable characteristics. Although narrowly sized ( $\approx 0.2 \mu\text{m}$ ) and equiaxed, it is strongly agglomerated. Some particles are also multinuclear aggregates which presumably formed during nucleation and growth. Little further characterization was done on this powder because of its undesirable characteristics. Further discussion of pure zirconia powders therefore refers to the *n*-propoxide derived zirconia unless otherwise stated.

The initial YSZ powders made by hydrolysis in isopropanol were also heavily agglomerated (see Fig. 4). However subsequent YSZ powders made by hydrolysis in ethanol are spheroidal, narrowly sized ( $\approx 0.2 \mu\text{m}$ ), unagglomerated particles which are virtually identical to the *n*-propoxide derived zirconia. Again, the excellent reproducibility of the YSZ powders is illustrated by Figs. 5 and 6 and by Fig. 2(B) in Fegley and Barringer.<sup>10</sup> The latter micrograph is of a separate batch made at a different time than the powder shown in Figs. 5 and 6. A TEM micrograph of the YSZ powder (Fig. 7) confirms the spheroidal shape of the powder.

Quantitative size distributions for seven different batches of zirconia powders are given in Table II. To a good first approximation, all batches are monodisperse ( $\sigma_z = 1.17$  to 1.24 where  $\sigma_z = 1 + \sigma/\bar{d}$ ;  $\bar{d}$  = mean size). Furthermore, the reproducibility, which is qualitatively illustrated in the SEM and TEM micrographs, is quantitatively demonstrated by these data to be  $\pm 20\%$  (based on dividing the range (52 nm) by the mean size (254 nm) of all 7 batches). Similar results were obtained for the YSZ powders; two different batches which were studied had essentially monodisperse particle size distributions of  $225 \pm 43 \text{ nm}$  and  $230 \pm 53 \text{ nm}$ .

#### Physical Properties

Table III summarizes the physical property measurements for the zirconia and YSZ powders; preliminary results and brief descriptions of the specific surface area and density measurements were given by Fegley and Barringer.<sup>10</sup>

The surface areas of the water washed zirconia powders were

dependent on the aging time. Thus, surface areas for samples aged for 3 to 10 d were in the range of  $\approx 112$  to  $136 \text{ m}^2/\text{g}$ , samples aged for 28 to 57 d had surface areas in the range of  $\approx 28$  to  $58 \text{ m}^2/\text{g}$ . By contrast the surface areas for ethanol washed zirconia were in the range of  $\approx 9$  to  $18 \text{ m}^2/\text{g}$ . Only three samples were measured and no trend with aging time was apparent in the data.

Larger surface areas were also observed for titania<sup>8</sup> and doped titania<sup>9</sup> powders washed in water instead of alcohol. Barringer<sup>16</sup> originally suggested that the larger surface areas resulted from a surface coating of fine spherical precipitates formed by the rapid hydrolysis of residual (unreacted) titanium ethoxide on the particle surface upon contact with water in the initial washing step. An analogous effect was suggested as the cause of the higher surface areas of water washed zirconia.<sup>10</sup> If this explanation is correct, coarsening of the surface precipitates during aging may be responsible for the observed decrease in surface areas. However, recent TEM micrographs do not show a difference between the surfaces of water washed and ethanol washed particles from the same batch of powder. An alternative suggestion is that the larger surface areas of the water washed powders are due to internal porosity which may be reduced or sealed off in the ethanol washed zirconia. However, the present data cannot distinguish between 'solid' zirconia particles or 'porous' spheroidal aggregates of smaller subunits. Finally, surface areas for water washed YSZ powders are in the range of  $\approx 66$  to  $84 \text{ m}^2/\text{g}$ . No aging study was done and no ethanol washed powders were studied.

The 'as-made' powders were amorphous as determined by X-ray diffraction. Pure zirconia powders calcined at  $\approx 600^\circ\text{C}$  for 4 h were monoclinic. Calcined YSZ powders were a mixture of non-transformable tetragonal and cubic phases. This is in agreement with the work of Miller et al.<sup>17-18</sup> on plasma-sprayed YSZ and with the yttria-zirconia phase diagram determined by Scott.<sup>19</sup>

#### Chemical Analyses

Extensive chemical analyses were done to determine cation impurity levels, the yttria dopant level in the YSZ powders, the

Table II. Zirconia Particle Size Distribution as Determined by Dynamic Laser Light Scattering

| Sample No. | Mean diameter, $\bar{d} \pm 1\sigma$ (nm) | $\sigma_z^*$ |
|------------|---|--------------|
| 16         | $223 \pm 38$                              | 1.17         |
| 9          | $240 \pm 53$                              | 1.22         |
| 13         | $252 \pm 65$                              | 1.26         |
| 17         | $256 \pm 55$                              | 1.21         |
| 12         | $260 \pm 52$                              | 1.20         |
| 10         | $274 \pm 64$                              | 1.24         |
| 14         | $275 \pm 66$                              | 1.24         |

\* $\sigma_z = 1 + \sigma/\bar{d}$ .

Table III. Physical Properties of Zirconia and Yttria-Stabilized Zirconia

| Property  | Type of powder             |                            |
|---|----------------------------|----------------------------|
|   | Pure zirconia              | Yttria-stabilized zirconia |
| Apparent surface area ( $\text{m}^2/\text{g}$ ) | 9-18*, 30-136 <sup>†</sup> | 66-84 <sup>†</sup>         |
| Density ( $\text{g}/\text{cm}^3$ )              |                            |                            |
| Precipitated powder                             | 2.9                        |                            |
| Calcined powder                                 | 5.0-5.3                    | 6.2                        |
| Crystallinity                                   |                            |                            |
| As-made powder                                  | Amorphous                  | Amorphous                  |
| Calcined powder                                 | Monoclinic                 | Tetragonal + cubic         |
| Weight loss from TG curve (%)                   | $\approx 20$               | $\approx 20$               |

\*Ethanol washed. <sup>†</sup>Water washed.





larger grain size and higher porosity relative to the sintered powder compacts are readily apparent. Qualitatively similar microstructures are produced by identical processing of *n*-propoxide derived zirconia. However, no detailed studies were done on "conventional" processing of the monodispersed powders. The preferential sintering of agglomerated powders is shown in Fig. 11. In this case, the agglomerated regions in a powder compact sintered faster than the surrounding areas and pulled away from them.

### Summary

The *controlled* hydrolysis of alkoxides is a comparatively simple, yet very powerful technique for controlling the size, shape, size distribution, and state of agglomeration of zirconia powders. The formation of zirconia and yttria-stabilized zirconia powders by this technique yields spheroidal ( $\approx 0.2 \mu\text{m}$ ), narrowly sized ( $\sigma_z = 1.17$  to 1.24), unagglomerated particles. These particles have been characterized by a variety of physical and chemical techniques.

The as-made particles are amorphous, and may be 'solid' spheres or 'porous' aggregates of smaller subunits. They have high chemical purity and can be manufactured reproducibly. Furthermore, the particles can be formed into uniformly dense ( $\rho \approx 65\% \rho_{th}$ ) green microstructures by controlling the pH of an aqueous powder dispersion. Sintering such uniformly packed microstructures can be done at temperatures as low as 1160°C. The resulting sintered microstructure is composed of uniformly sized ( $\bar{d} \approx 0.2 \mu\text{m}$ ) grains and is >98% of theoretical density. Experiments also show that similarly sized particles do not sinter to as desirable microstructures if the particles are heavily agglomerated.

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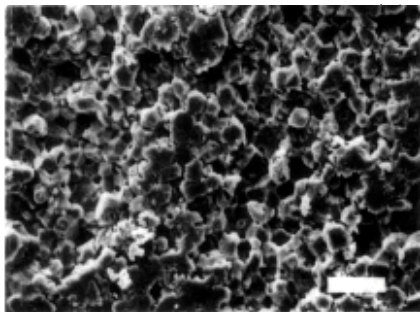
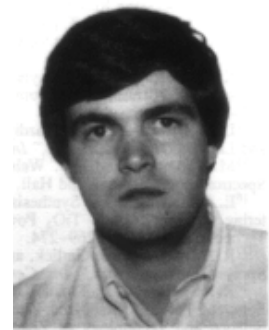


Fig. 10. Scanning electron micrograph of fracture surface of zirconia ceramic sintered at 1500°C for 4 h; initial sample was isopropoxide zirconia (see Fig. 3) which was die-pressed and isostatically pressed (bar=5  $\mu\text{m}$ ).



Bruce Fegley, Jr.



Paul White

**Bruce Fegley, Jr.** is a principal research scientist in the Dept. of Earth, Atmospheric, and Planetary Sciences at Massachusetts Institute of Technology. He received an S.B. in chemistry in 1975 and a Ph.D. in geochemistry in 1980, both from MIT. During 1980-82 he was a postdoctoral research associate at the Harvard College Observatory, and during 1982-84 he was a postdoctoral associate in the Materials Processing Center at MIT.

**Paul White** is a research specialist in the Materials Processing Center at MIT. He graduated from the University of Massachusetts, Amherst in 1982 with an S.B. in chemical engineering.

**H. Kent Bowen** is Ford Professor of Engineering in the Depts. of Materials Science and Engineering and Electrical Engineering and Computer Science at MIT. He also serves as director of the Materials Processing Center. Dr. Bowen earned his B.S. in ceramic engineering from the University of Utah in 1967 and his Ph.D. from MIT in 1971. He has been a member of the faculty since 1970.



H. Kent Bowen

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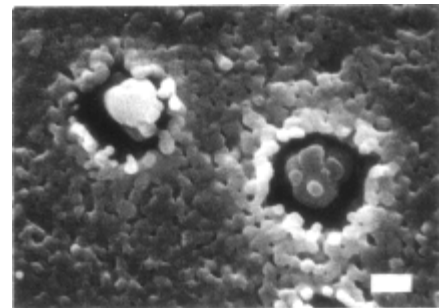


Fig. 11. Scanning electron micrograph of top surface of zirconia ceramic. Agglomerated regions in powder compact sintered faster than surrounding areas and pulled away from them.

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