

Preparation of Zirconia-Alumina Powders by Zirconium Alkoxide Hydrolysis

BRUCE FEGLEY, JR.,** PAUL WHITE,* AND H. KENT BOWEN*

Materials Processing Center, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Zirconia-alumina powders were prepared by controlled hydrolysis of zirconium propoxide in a dispersion of α -alumina powder in anhydrous 100% ethanol. Transmission electron micrographs show a "fluffy" zirconia coating on the alumina particles. Chemical analyses by four methods demonstrated that the procedure is reproducible and introduces only low impurity levels.

RECENT interest in designing transformation-toughened ceramics such as zirconia-toughened alumina, mullite, and spinel has led to the development of several ways for producing these materials.¹ The methods, including mechanical mixing of powders,¹ attrition milling of zirconia grinding media,¹ sol-gel syntheses,^{1,2} reactive sintering,¹ and evaporative decomposition of slurries,³ attempt to control the chemistry and microstructure of sintered ceramics and thereby their mechanical properties. Specifically, toughening resulting from stress-induced transformation or microcrack nucleation may be optimized by minimizing zirconia particle size and size distribution.¹ Also, maintaining tetragonal zirconia is essential for stress-

induced transformation toughening, whereas a uniform zirconia particle distribution is important for optimizing microcrack nucleation-induced toughening.¹

The present report describes a new zirconia-alumina powder preparation technique involving hydrolysis of a zirconium alkoxide in an α -alumina dispersion. If the alumina particles are small and have a narrow size distribution, the resulting zirconia-alumina particles are also small and narrow. The techniques described herein are advantageous over conventional techniques such as mechanical mixing because they yield powders that are small, narrow in size, and of controlled chemical composition. Such "ideal" powders, which arguably possess intrinsic processing advantages over commercial powders,^{4,5} may permit better design of zirconia-toughened ceramics.

EXPERIMENTAL PROCEDURE

Controlled hydrolysis of zirconium propoxide, $Zr(OC_3H_7)_4$, in a powder dispersion was used to prepare zirconia-alumina, zirconia-mullite, and zirconia-spinel powders. Both zirconium *n*-propoxide[†] and isopropoxide[†] were used in experiments;

however, results reported are for powders prepared from zirconium *n*-propoxide only. Commercial α -alumina,[‡] mullite,[§] and spinel[¶] powders were used as well as narrow-sized, 0.25- μ m-diameter α -alumina powder prepared by centrifugal separation of particles into size classifications.⁶ All hydrolysis reactions were done in a glove box in a dry N_2 atmosphere.

In a typical experiment to synthesize zirconia-alumina powder, several grams of dry alumina powder were ultrasonically dispersed in anhydrous 100% ethanol by a process similar to that used in centrifugal sizing of α -alumina powder.⁶ This dispersion was thoroughly mixed with a solution of $Zr(OC_3H_7)_4$ in anhydrous 100% ethanol and heated to 50°C. The resulting powder/alkoxide dispersion was hydrolyzed by adding to it a slightly smaller volume of a deionized water/ethanol solution, also at 50°C, while stirring. No precipitation could be observed because the dispersion was initially cloudy white.

After the dispersion was mixed for several minutes, it was centrifuged to remove the ethanol solution. The zirconia-alumina powder product was washed twice with deionized water in a redispersion-centrifuging cycle and dried at 80°C.

Chemical and physical properties were measured by several methods. Several powder samples were also dry-pressed at 31 MPa and then isostatically pressed at 276 MPa. These "pills" were sintered at 1500 to 1600°C in air for 4 to 5 h before electron probe microanalysis (EPMA).

Reactant amounts used in the experiments varied with the desired composition of the zirconia-alumina powder. Typically, the powder/alkoxide dispersion contained 4 to 8 g of α -alumina and had a total volume of \approx 800 mL. The initial concentration of $Zr(OC_3H_7)_4$ in the dispersion was \approx 0.02 to 0.10M; initial concentration of the deionized water solution was \approx 0.2 to 1.5M.

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*Member, the American Ceramic Society.

**Present address: Department of Earth, Atmospheric and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139.

†Alfa Products, Danvers, MA.

‡XA139SG Alumina, Aluminum Co. of America, Pittsburgh, PA.

§High-purity mullite and spinel, Baikowski Intl. Corp., Charlotte, NC.

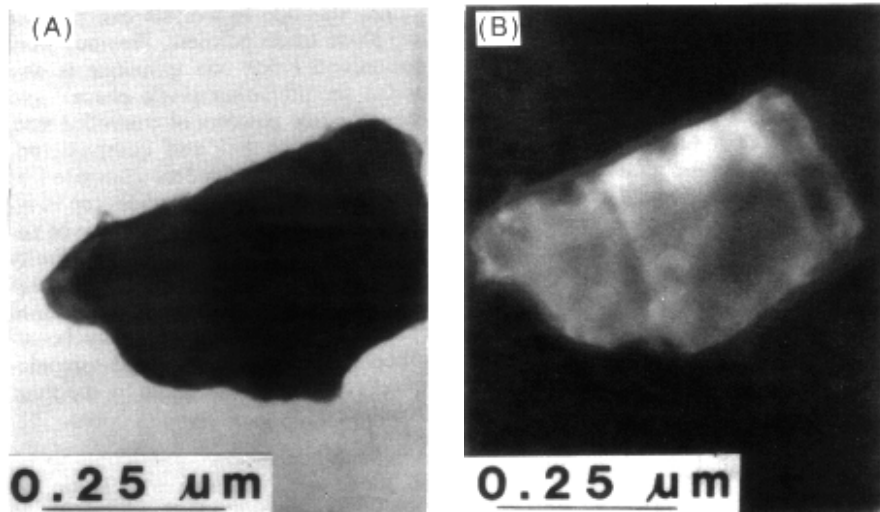


Fig. 1. Transmission electron micrographs of zirconia-alumina powder, showing (A) bright-field and (B) dark-field images of same particle.

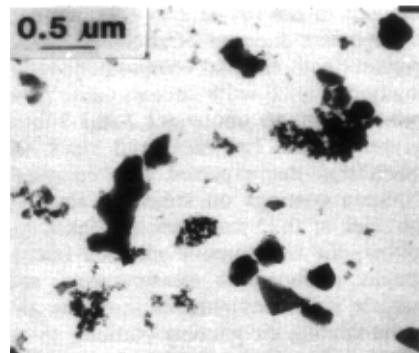


Fig. 2. Transmission electron micrograph of physical mixture of alumina powder and alkoxide-derived zirconia powder. Most of the zirconia occurs in aggregates separate from alumina particles (photo courtesy of W. C. Moffatt and B. Novich).

Table I. Batch-to-Batch Chemical Reproducibility of Zirconia-Alumina Powders

Sample No.	Zirconia content (wt%)	Analytical method
1	26.5±0.5	Wet chemistry
2	27.0±1.8	PIXE*
3	27.2±1.3	EPMA [†]
4	28.1±0.6	EPMA

*Proton-induced X-ray emission. [†]Electron probe microanalysis.

The water/alkoxide molar ratio was usually 10, but it varied from 5 to 20 in the experiments.

Zirconia-mullite and zirconia-spinel powders were prepared by using similar amounts of reactants and were processed by the same methods. However, only chemical analyses by EPMA were conducted on these ceramics.

RESULTS AND DISCUSSION

Figures 1(A) and (B) show bright-field and dark-field transmission electron micrographs of zirconia-alumina powder. These figures, representative of zirconia-alumina powders made from size-sorted α -alumina powder, clearly show that zirconia is coating individual alumina particles and is not just physically mixed with them. The latter situation, which is illustrated in Fig. 2, may result when alumina powder and zirconium propoxide are not mixed well before hydrolysis.⁷

Further information about the zirconia coating on alumina particles was obtained from physical property measurements. Surface areas were measured by a multipoint BET⁹ method using N₂ gas as the adsorbate and assuming a cross-sectional area of 1.62 nm². The values range from ≈ 12 m²/g (equivalent spherical diameter = 0.12 μ m) for the sized alumina powder to ≈ 100 m²/g for zirconia-alumina powder with a nominal composition of 20 vol% zirconia. The apparent (hydrodynamic) sizes of the α -alumina and zirconia-alumina powders were measured by dynamic laser-light scattering (photon correlation spectroscopy).^{**} The apparent diameter of the size-sorted α -alumina powder is 0.25 μ m ($\sigma_z=1.2$ to 1.3), whereas the apparent diameter of zirconia-alumina powders with nominal compositions ranging from 4 to 20 vol% zirconia varies from ≈ 0.34 to ≈ 0.40 μ m ($\sigma_z=1.2$ to 1.3 for a given batch). The measured sizes are much larger than expected from "compact" zirconia coatings on spherical alumina particles of 0.25 μ m diameter. Taken together, the transmission electron micrographs, surface area measurements, and particle size measurements show the zirconia coating on alumina particles to be "fluffy" in nature. Furthermore, X-ray diffraction shows the zirconia to be amorphous.

⁹Quantasorb, Quantachrome Corp., Syosset, NY.

^{**}Model N4D, Coulter Electronics, Inc., Hialeah, FL.

Table II. Representative Impurity Levels in Zirconia-Alumina Powders

Method	Amount (ppm)*			
	CaO	FeO	SiO ₂	TiO ₂
ICP	54±9	130±30	1020±560	2400±700
EPMA	300±100	800±500	2500±1400	NA
PIXE	270±70	160±10	ND	3000±520

*NA—not analyzed; ND—not detected.

The zirconia-alumina powders and ceramics were analyzed by electron probe microanalysis, inductively coupled plasma emission spectroscopy (ICP), proton-induced X-ray emission (PIXE),^{††} and wet chemistry. Back-scattered electron imaging on a scanning electron microscope was also used to characterize the ceramics. The EPMA data are from a probe^{‡‡} operated at 15 kV and 30 nA. Well-characterized standards at the Department of Geological Sciences, Harvard University, were used in the analyses. Descriptions of the ICP and PIXE techniques are given by Thompson and Walsh⁸ and Burnett and Wollum,⁹ respectively, and will not be reported in the present paper.

The chemical analyses illustrate that the controlled alkoxide hydrolysis technique is versatile, producing zirconia-alumina powders containing ≈ 8 to 28 wt% zirconia. The analytical data in Table I, which are from EPMA, PIXE, and wet chemistry, show that batch-to-batch chemical reproducibility is very good. Furthermore, the data in Table I show good agreement between the results of the different analytical methods.

Representative impurity levels in zirconia-alumina powders are shown in Table II. The major impurities are CaO, FeO, SiO₂, and TiO₂. The ICP analyses for 25 other cations (As, B, Ba, Be, Cd, Co, Cr, Cu, Ga, La, Li, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sn, Sr, V, Zn, and K) show no other impurities at levels above 20 ppm. The high TiO₂ levels are almost certainly due to contamination from the Ti tip of the ultrasonic probe used to disperse powder during washing. The origin of the SiO₂ impurity is more obscure—it is probably a combination of SiO₂ from the glassware, alumina powder, and zirconium alkoxide. The similar SiO₂ impurity level in alkoxide-synthesized, doped titania powders¹⁰ indicates that more stringent precautions, such as alkoxide purification and/or elimination of glassware for reactions, are needed to reduce this impurity.

Back-scattered electron images show that the sintered zirconia-alumina ceramics are homogeneous on length scales from ≈ 5 to ≈ 1000 μ m. The EPMA results for analyses done 1 to 2 mm apart show that the ceramics are also homogeneous on scales up to the sample size of ≈ 10 mm. Zirconia and alumina grain sizes, visually estimated from back-scattered electron micrographs, are 1 to 2 μ m. Thus, the

Table III. Chemical Composition of Zirconia-Mullite and Zirconia-Spinel Ceramics as Determined by Electron Probe Microanalysis

Oxide	Amount Present (wt%)*	
	Zirconia-mullite	Zirconia-spinel
ZrO ₂	8.12	16.32
Al ₂ O ₃	63.78	58.00
SiO ₂	27.55	0.15
MgO	NA	24.16
CaO	0.22	0.86
TiO ₂	0.28	NA
FeO	NA	<0.03
Total	99.95	99.49

*NA—not analyzed.

alkoxide-produced zirconia-alumina powders yield fine-grained, compositionally uniform ceramics.

Two of the EPMA samples were also examined by X-ray diffraction using CuK α radiation. The monoclinic phase was identified from the (111) and (111) peaks at $\approx 28.3^\circ$ and $\approx 31.5^\circ$, respectively. The tetragonal phase was identified by the (111) peak at $\approx 30.3^\circ$. Other peaks of the monoclinic and tetragonal phases were also found.

Finally, zirconia-mullite and zirconia-spinel ceramics were analyzed by EPMA. The analytical results (Table III) show that mullite and spinel ceramics with a range of zirconia contents can be synthesized by the controlled-hydrolysis technique. However, further analyses are needed to establish these compositions, reproducibly, and to define the major impurities and their levels.

CONCLUSIONS

The present study demonstrates that controlled alkoxide hydrolysis can produce two-phase oxide powders. Previous work demonstrated that this technique is also useful for preparing single-phase¹¹ and doped¹⁰ oxide powders of controlled size, size range, shape, and composition. Zirconia-alumina powders composed of zirconia-coated alumina particles can be reproducibly synthesized with a range of zirconia contents and generally low impurity levels. Furthermore, sintered ceramics made from these powders are fine-grained (1 to 2 μ m) and compositionally homogeneous. Zirconia-mullite and zirconia-spinel ceramics can be made by the same techniques.

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^{††}Element Analysis Corp., Tallahassee, FL.

^{‡‡}Cameca MBX, Cameca Corp., Los Angeles, CA.

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