Processing and Characterization of ZrO$_2$ and Y-Doped ZrO$_2$ Powders

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Monodisperse spheroidal zirconia and yttria-stabilized zirconia particles with an average diameter of ≈0.2 μm 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.

Historically, a great deal of effort was spent on the synthesis of small-particle-size ceramic powders.[1-3] The apparent desirability of these powders, which may be ≤1.0 μm in size, was based on the greatly enhanced sintering kinetics which were predicted for fine powders.[4] 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.[3,5] 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).[6]

One method for controlling important powder characteristics such as size, shape, size distribution, and state of agglomeration is the *controlled* hydrolysis of metal alkoxides.[7-10] 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.[1] 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.[8-11]

Barringer and Bowen[8] recently demonstrated that the controlled hydrolysis of titanium alkoxides gave monodisperse TiO$_2$ powders which could be sintered to 99+% of theoretical density at temperatures several hundred degrees lower than those required to sinter conventional TiO$_2$ powders. Their success parallels Rhodes'

success in sintering specially prepared yttria-stabilized zirconia (YSZ) powders at temperatures several hundred degrees lower than agglomerated zirconia powders.[5] These two demonstrations and Mazdiyasni's work[1] 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[10] 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
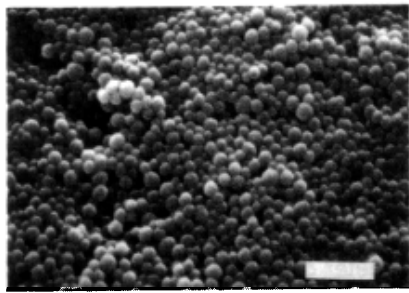

Fig. 1. Scanning electron micrograph of undoped zirconia made by controlled hydrolysis of zirconium n-propoxide in January 1983 (bar=1 μm).

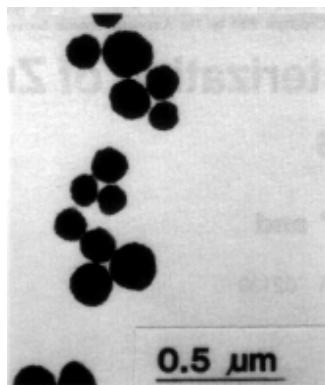

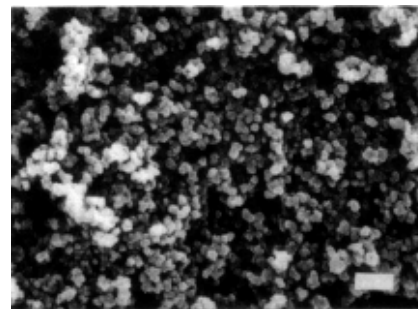Fig. 2. Transmission electron micrograph of undoped zirconia (n-propoxide derived, water-washed).

Fig. 3. Scanning electron micrograph of undoped zirconia made from zirconium isopropoxide in July 1983 (bar=1 μm).

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. Mazdiyasni et al.[12] 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 Mazdiyasni's procedures.[13-14] 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,[10] 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[†] 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.[‡] Specific surface areas of the powders were measured by N_2 gas adsorption (multi-point BET method.)[§] Powder densities were measured by a stereopycnometer[∥] using He gas. Crystallinity was determined by powder X-ray diffraction using CuKα 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).[15] Ceramics were analyzed by wet chemistry, proton induced X-ray emission (PIXE),[††] and electron probe microanalysis (EPMA).[‡‡] 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 ≈0.2 μm 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,[10] which are SEM micrographs of pure zirconia synthesized in July 1983. (Note: Figures 4(A),(B) and 5(A),(B) in Fegley and Barringer[10] 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)	n-Propoxide	Isopropoxide	Y(^{i}OC₃H₇)₃ and Zr(^{n}OC₃H₇)₄
Alkoxide concentration (M)	0.1	0.1	0.08 (Zr) 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 (%)	≈60	≈95	≈60*

*Yield of 45% given in Ref. 10 represents hydrolysis in dry isopropanol done by Dr. H. Okamura.
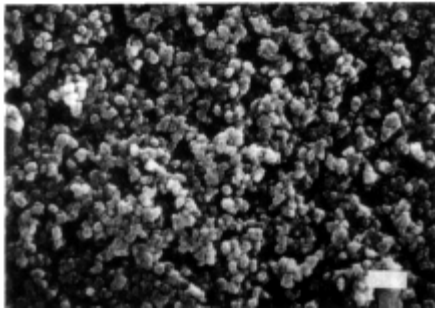
Fig. 4. Scanning electron micrograph of yttria-stabilized zirconia powder made by hydrolysis in isopropanol (bar=1 μm).
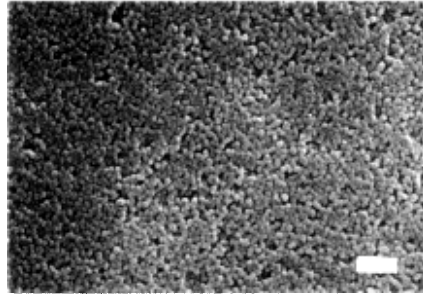
Fig. 5. Scanning electron micrograph of yttria-stabilized zirconia made by hydrolysis in ethanol (top surface of gravity-sedimented compact) (bar=1 μm).
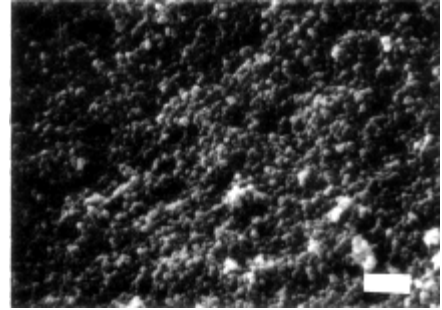
Fig. 6. Scanning electron micrograph of fracture surface of yttria-stabilized zirconia compact shown in Fig. 5 (bar=1 μm).

of zirconia made in August 1984 and Fig. 1(B) of Fegley and Barringer[10] 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 μm) 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 μm), 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.[10] 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 $\pm20\%$ (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 ± 43 nm and 230 ± 53 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.[10]

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 m^2/g, samples aged for 28 to 57 d had surface areas in the range of $\approx$28 to 58 m^2/g. By contrast the surface areas for ethanol washed zirconia were in the range of $\approx$9 to 18 m^2/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[8] and doped titania[9] powders washed in water instead of alcohol. Barringer[16] 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.[10] 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 m^2/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°C for 4 h were monoclinic. Calcined YSZ powders were a mixture of nontransformable tetragonal and cubic phases. This is in agreement with the work of Miller et al.[17-18] on plasma-sprayed YSZ and with the yttria-zirconia phase diagram determined by Scott.[19]

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)	σ_z*
16	223±38	1.17
9	240±53	1.22
13	252±65	1.26
17	256±55	1.21
12	260±52	1.20
10	274±64	1.24
14	275±66	1.24

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

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

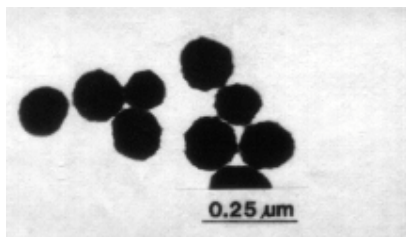| Property	Type of powder	
	Pure zirconia	Yttria-stabilized zirconia
Apparent surface area (m^2/g)	9–18*; 30–136[†]	66–84[†]
Density (g/cm^3)		
Precipitated powder	2.9	
Calcined powder	5.0–5.3	6.2
Crystallinity		
As-made powder	Amorphous	Amorphous
Calcined powder	Monoclinic	Tetragonal+cubic
Weight loss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

*Ethanol washed. [†]Water washed.

Fig. 7. Transmission electron micrograph of yttria-stabilized zirconia made by hydrolysis in ethanol.
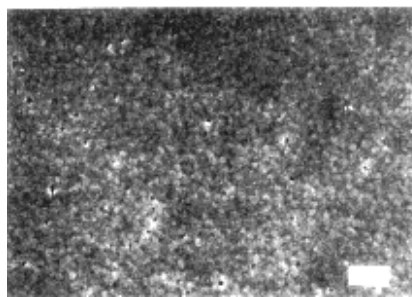
0.25 μm

Fig. 8. Scanning electron micrograph of top surface of yttria-stabilized zirconia ceramic sintered at 1240°C for 20 min (constant heating rate of 20°C/min) (bar=1 μm).
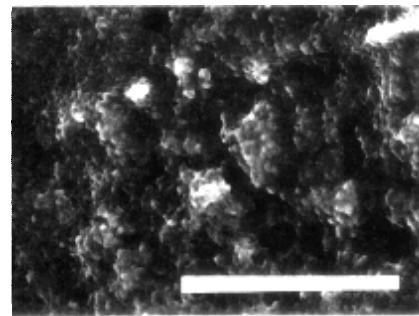

Fig. 9. Scanning electron micrograph of fracture surface corresponding to Fig. 8 (bar=10 μm).

reproducibility of the doping technique, and the carbon content of the as-made powders. Impurities in the zirconia and YSZ powders are listed in Table IV. The major cation impurities are Fe (100 to 200 ppm), Si (60 to 400 ppm), Ti (~350 ppm), and Hf (~1.3%). All other elements analyzed are present below detection limits. The Ti impurity, which is also seen in alkoxide derived zirconia-alumina powders,[20] may be due to contamination from the Ti tip on the ultrasonic probe used to disperse the powders during processing. The Si impurity, also common in other alkoxide derived powders,[10] may be from the bottles used to store the alkoxides or from glassware used for the hydrolysis reactions. The Hf impurity is present only in zirconia and YSZ powders made from the n-propoxide. The isopropoxide derived powders contain <100 ppm Hf as determined by ICP and PIXE.

The composition of the YSZ ceramics is 15.8 mol% $YO_{1.5}$; the reproducibility of the yttria dopant and hafnia impurity levels are compared in Table V. Finally, carbon analyses of the water washed zirconia made from the n-propoxide showed 1.02% to 1.07% carbon. This is presumably due to residual alkoxide and trapped alcohol, and is consistent with the DTA-TG results.

Dispersion, Packing, and Sintering

General guidelines for the dispersion and packing of fine, narrowly sized powders were reviewed by Fegley and Barringer.[10] Basically, the goal of these operations is to control particle packing in green microstructures, and thus control sintered microstructures and properties.

A YSZ powder compact is illustrated in Figs. 5 and 6 and a zirconia compact is shown in Figs. 4(A) and 4(B) in Fegley and Barringer.[10] These four SEM micrographs are representative of the packing in the powder compacts. The uniformity, as determined by SEM, is maintained over the entire sample. The typical void size

observed is ≈2 to 3 particle diameters. Densities of the powder compacts were estimated as ≈65% ρ_{th} by using the equation

$$\rho/\rho_{th}=\rho_o/\rho_{th}[1-\Delta l/l_o]^{-3} \qquad (1)$$

where ρ_o/ρ_{th} was the initial (green) density, $\Delta l/l_o$ was the total relative shrinkage from dilatometry,[88] and ρ/ρ_{th} was the relative density of the sintered compact.[16] The relative density of the sintered compacts was estimated from SEM micrographs of as-sintered and fracture surfaces of compacts by using standard techniques.[21-22] (The dilatometry data are described in detail in a paper on zirconia sintering (Fegley and White, in preparation).)

Sintering in air was done for various times at temperatures from 1050° to 1500°C. The qualitative results of these experiments show that the uniformly packed compacts sintered to relatively dense ($\rho>98\%$ ρ_{th}), uniform, fine-grained ($\bar{d}$ ≈0.2 to 0.4 μm) ceramics. Fegley and Barringer[10] showed a sample of zirconia which was sintered at 1160°C for 1.5 h to such a microstructure (Figs. 6(A) and (B)). This result was reproduced and confirmed in the present work. Figures 8 and 9 show the top and fracture surfaces, respectively, of a YSZ ceramic sintered at 1240°C for 20 min. This ceramic also has a relatively uniform, fine-grained ($\bar{d}$ ≈0.2 to 0.4 μm) microstructure with low porosity (~2%). These examples (and other SEM micrographs) show that uniformly packed powder compacts of zirconia and YSZ sinter to $\rho>98\%$ ρ_{th} at temperatures hundreds of degrees lower than conventional powders.[3,23] The resulting microstructures are also more uniform and finer-grained than conventional microstructures. Although extensive quantitative data are required for a detailed understanding, the qualitative comparisons can be made from these microstructures and those of Fegley and Barringer[10] to the microstructures illustrated in the literature using conventional powders.[23-31]

However, these desirable microstructures from ideal powders are not obtained if the green microstructure is not controlled. Figure 10, which shows the fracture surface of a ceramic sintered at 1500°C for 4 h, helps to illustrate this point. The initial sample was isopropoxide derived zirconia which was dry-pressed uniaxially at 31 MPa and then isostatically pressed at 276 MPa. The

§§Model 402E, Netzch Corp., Exton, PA.

Table IV. Representative Impurity Levels in Alkoxide-Derived Zirconia as Determined by Inductively Coupled Plasma Emission Spectroscopy

Element	Amount (ppm)	Element	Amount (ppm)
Al	<160	Mo	<20
As	<50	Na	<50
B	<20	Nb	<100
Be	<10	Ni	<30
Ca	<20	P	<50
Cd	<10	Pb	<50
Co	<10	Sb	<50
Cr	<30	Si	60–400
Cu	<20	Sn	<50
Fe	100–200	Sr	<10
Ga	<50	Ta	<100
Gd	<60	Ti	≈350
La	<20	V	<20
Mg	<10	Zn	<20
Mn	<10	Hf	≈1.3%*

*See text.

Table V. Chemical Reproducibility of Y_2O_3-Doped ZrO_2 Ceramics

| Sample No. | Weight ratio | | Method |
	ZrO_2/Y_2O_3	ZrO_2/HfO_2	
1	5.77±0.04	47.8±0.6	EPMA*
2	5.74±0.12	49.0±0.5	EPMA
3	6.28±0.73	50.8±0.7	Wet chemistry

*Electron probe microanalysis.

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 (≈ 0.2 μm), 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 ($\rho \approx 65\%$ ρ_{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 ($\bar{d} \approx 0.2$ μm) 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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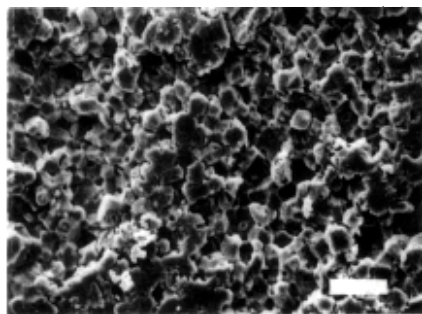
Fig. 10. Scanning electron micrograph of fracture surface of zirconia ceramic sintered at 1500°C for 4 h; initial sample was isopropoxide zirconia (see Fig. 3) which was die-pressed and isostatically pressed (bar=5 μm).
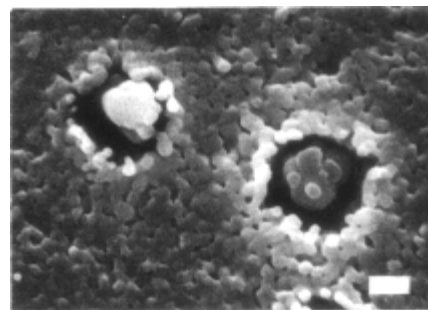

Fig. 11. Scanning electron micrograph of top surface of zirconia ceramic. Agglomerated regions in powder compact sintered faster than surrounding areas and pulled away from them.

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