OPTIMISATION OF Y_2O_3 DOPED ZrO_2 POWDER (Y-TZP)

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Abstract

Fine sinteractive Y-TZP powder, produced by a conventional wet chemistry process, has been optimised to give a strong, dense and tough ceramic. Very high conductivity has also been achieved.

Introduction

The requirements for optimum mechanical properties[1] of 2 to 3 mole% Y_2O_3 doped Zirconia (Y-TZP) are now clear.

Green bodies made up of uniformly distributed submicron particles are required [2,3] if the necessary high sinteractivity is to be achieved.

For conductivity at elevated temperatures very high purity powders[4] which have a low grain boundary resistivity are required[4].

There is a considerable technological challenge in producing powders which meet these very demanding requirements without recourse to the cost of such techniques as sol gel processing for example.

This paper describes the preparation of such powders which make up the Z-TECH SY-ULTRA range.

The powder is produced by calcination of a chemically coprecipitated intermediate. It is then milled and spray dried. The latter part of the process will be discussed.

The process produces a powder with a very uniform Yttrium distribution. A new method of measuring the uniformity of Yttrium distribution in Zirconia has been developed[5].

Milling

The calcined Y_2O_3 doped Zirconia Powder consists of agglomerates approximately 25 microns in size consisting of tetragonal crystallites. Comminution of this material was investigated initially by ball milling in laboratory test apparatus as follows:

Polypropylene Jar Height 6 cm Diameter 7 cm
290g 3 mm diameter Y-TZP Balls
rotation speed 120 r.p.m.
slip volume 33 ml (eg. for 50% wt. slip, 28g powder + 28 ml water plus dispersant)
milling time 24 hours (unless otherwise stated)

The first experiments were carried out without dispersant (see Table 1).

TABLE 1

Slip Concentration (wt.% ZrO_2)	Particle Size (microns) *		
	10%	50%	90%
4	0.26	0.70	2.23
8	0.19	0.43	1.44
12	0.18	0.42	1.33
20	0.21	0.54	1.49
50	0.27	1.66	4.38

* Measured with a Leeds and Northrup MICROTRAC

The smallest particle size was obtained with a 12% wt. slip. No further size reduction was observed after 24 hours.

Next the effect of a dispersant (Dispex A40 Allied Colloids) an ammonium acrylate polymer was investigated. (see Table 2)

TABLE 2

Slip Concentration (wt.% ZrO_2)	Dispex-A40 (g/100g ZrO_2)	Particle Size (microns)		
		10%	50%	90%
30	1.0	0.13	0.33	0.80
	2.0	0.13	0.33	0.82
40	1.0	0.13	0.35	0.84
	2.0	0.13	0.30	0.65
50	0.1	0.25	1.01	3.20
	0.5	0.13	0.39	0.96
	1.0	0.13	0.29	0.65
	2.0	0.13	0.29	0.69
60	1.0	0.13	0.41	1.01
	2.0	0.13	0.37	0.88
70	2.0	0.13	3.28	7.59

The smallest particle size was obtained with a 50% slip and 1% Dispex A40.

The effect of Powder Calcination temperature on milling rate and final particle size is given in Table 3. No significant differences were observed.

TABLE 3

Calcination Temperature (°C)	Particle Size (8 hr milling)*		Particle Size (24 hr Milling)*	
	50%	90%	50%	90%
775	0.53	1.64	0.34	0.73
825	0.54	1.77	0.35	0.63
925	0.54	1.73	0.34	0.66

* Milling Conditions : 50% Slip, 1% Dispex A40.

These experiments were used as a basis for scaling up to a pilot plant.

In production it has been found that an increase in milling rate can be achieved using an attritor mill using similar conditions to the ball milling described above. The properties of typical slips produced by this method are given in Table 4.

TABLE 4

Slip Concentration	60 to 70%
Particle Size	50% < 0.3 , 90% < 0.6 microns
Viscosity	5 to 10 mPa.s (Newtonian)

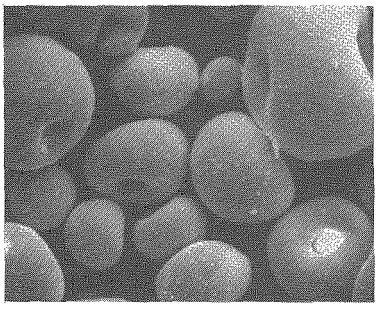
Spray Drying

A slip dispersed with Dispex A40 was spray dried on a Niro Production Minor spray dryer using an inlet temperature of 300°C and an outlet temperature of 105°C. Two products were collected, the major product, Powder A, with an agglomerate size of 30 microns (see Figure 1, A) and material from the cyclone, Powder B, with a size of 14 microns (see Figure 1, B).

Product Evaluation

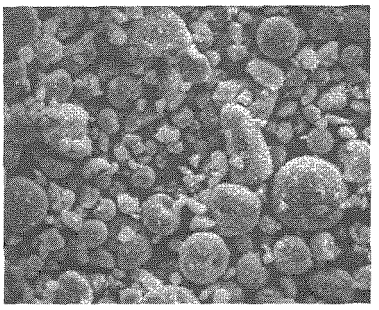
Powder A was uniaxially pressed at 20 MPa followed by isostatic pressing at 200 MPa. It was fired at 1500°C. A low sintered density and strength were obtained on the sintered product (Powder A, Table 5).

Figure 1A



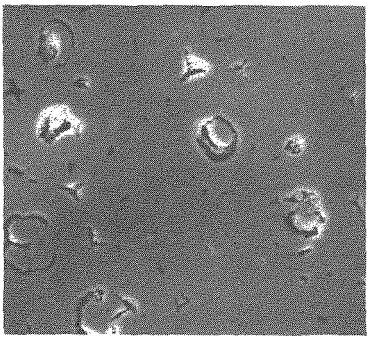
10 μm

Figure 1B



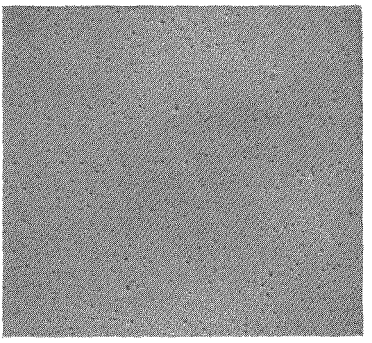
10 μm

Figure 2A



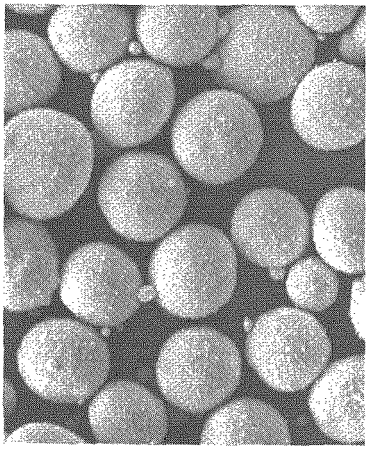
10 μm

Figure 2B



10 μm

Figure 3



100 μm

TABLE 5

POWDER	MEDIAN SPRAY DRIED AGGLOMERATE SIZE (Microns)	TAP DENSITY (g/ml)	FLOW TIME** (Sec.)		GREEN DENSITY (g/ml)	SINTERED DENSITY (g/ml)	MOR (MPa)+
			3mm	5mm			
A	24	1.89	67	23	3.25	5.94	733±59
B	14	2.00	*	65	3.26	6.04	954±90
SY-ULTRA	40	1.40	80	30	3.10	6.07	1110±151

* No Flow
** Measured on a Hall flowmeter
+ 4-Point Bend

S.E.M. examination of a ground and polished surface of the sintered body clearly shows the toroidal shape of the original spray dried agglomerates (see Figure 2, Powder A).

The fine fraction (Powder B) was evaluated in a similar manner. Considerably higher strength and density was obtained (see Table 5). S.E.M. examination (Figure 2, Powder B) showed fairly uniform fine porosity. This result is consistent with the pores between the spray dried agglomerates in compacts made from Powder B being smaller than in compacts made from Powder A.

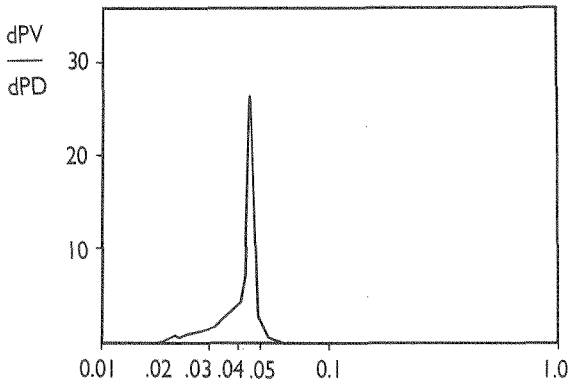
Unfortunately reducing the spray dried agglomerate size to that of Powder B is not an acceptable option because the bulk density is low and the flow properties are poor (see Table 5). Such a powder is very difficult to handle in dry pressing.

SY-ULTRA

The particle size, surface area and spray drying conditions for Powder B were optimized at the Pilot Plant scale. The poor flow properties however could not be overcome. Consequently a new product SY-ULTRA has been developed. It consists of spheroidal uniformly dense spray dried particles (see Figure 3). This weakly agglomerated powder deforms readily on pressing to give a uniform green body with high sinteractivity.

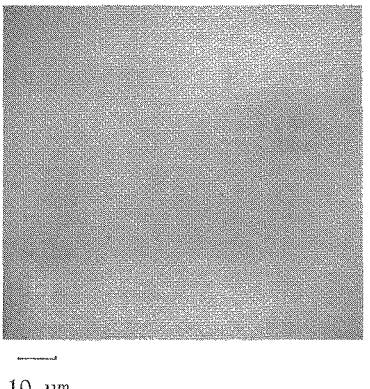
Mercury porosimetry shows a narrow pore size distribution in the green body (see Figure 4). A polished surface (see Figure 5) of the sintered body shows only an occasional small pore and excellent strength and density (see Table 5) are obtained.

FIGURE 4.



The pore size distribution of SY-ULTRA pressed and heated to 750°C.

Figure 5



Conductivity Studies

Yttria doped Zirconia is a solid electrolyte. This property is being used in oxygen sensors and several other applications are under development including, solid oxide fuel cells (SOFC), electrochemical reactors and oxygen pumps.

The resistivity of zirconia can be separated into components due to the lattice (within grains) and across interfaces (eg. grain boundaries). Grain boundary resistivity is generally very high, consequently large grained fully stabilized cubic zirconia has been used to minimise this effect. Recently however it has been demonstrated [6] that very high purity Y-TZP can achieve better conductivity than fully stabilized yttria-zirconia because the grain boundary resistivity has been reduced dramatically.

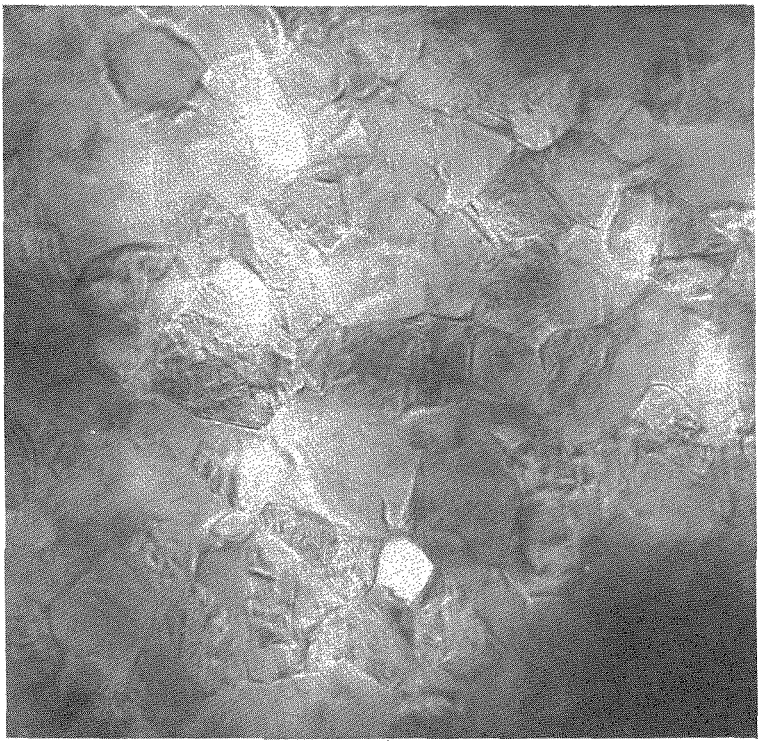
SY-ULTRA performs particularly well in this application[7].

Figure 6 shows a TEM of sintered SY-ULTRA. No glassy phase can be detected in the grain boundaries.

Acknowledgements

We would like to thank Dr. J. Sellar for the TEM results on SY-ULTRA and other members of the research team for their contributions to this work.

Figure 6



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