

# DEPENDENCE OF SINTERABILITY ON STATE OF AGGLOMERATION OF ULTRAFINE $\text{ZrO}_2(\text{Y}_2\text{O}_3)$ POWDERS<sup>①</sup>

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**ABSTRACT** The dependence of sinterability on the state of agglomeration of ultrafine  $\text{ZrO}_2(\text{Y}_2\text{O}_3)$  powders prepared by coprecipitation was investigated. The results showed that the powder prepared by direct drying and calcination of the water-washed gels was poorly sinterable with sintered density as low as 89% of theoretical value. The powder sinterability could be markedly improved by ball milling, and the sintered density could be increased to 96% of theoretical value under the same sintering conditions. Highly sinterable powders were prepared by adding some surfactants or by alcohol dehydration before gel drying, and the relative sintered densities greater than 98% were obtained. Sinterability mainly depended on the state of agglomeration of powders. The relation between sintered density and the state of agglomeration of powders was discussed.

**Key words** zirconia ultrafine powder agglomeration sinterability

## 1 INTRODUCTION

High quality powders are of fundamental importance in the successful fabrication of ceramic materials. Ultrafine powders derived from wet-chemical routes often contain hard agglomerates which are particularly detrimental to the final products. The effect of the state of agglomeration of ultrafine powders on the sinterability has received much attention<sup>[1-7]</sup>.

Haberko<sup>[1]</sup> showed that water-washed zirconium hydroxide gels produced hard agglomerates, whereas further washing with ethyl alcohol produced soft agglomerates. For a given consolidation pressure, the sintered density of the soft agglomerated powder at 1300 °C for 3 h was greater than 98% of theoretical density, while that of the hard one ranged between 82% and 86%. Haberko explained these results by suggesting that the soft agglomerated powder packed more uniformly.

Rhodes<sup>[2]</sup> showed that agglomerate-free powder, which was obtained by centrifugal sedimentation, could be centrifugally casted to 74% green density and sintered at 1100 °C for 1 h to 99.5% of theoretical density, whereas at least 1400 °C was necessary for agglomerated powder to be sintered to the same density.

Lange<sup>[3]</sup> studied the effect of the state of agglomeration on the sinterability from the point of view of the coordination number of pores in a compact of agglomerated powder.

Van de Graaf and Burggraaf<sup>[4]</sup> found abnormal grain growth due to the existence of agglomerates in a compact.

Dynys and Holloran<sup>[5]</sup> investigated the effect of the amount of agglomerates included in a compact on the sinterability.

Some other researchers<sup>[6,7]</sup> showed that sinterability could be improved by decreasing the agglomerate size.

The present work investigates the effect of the state of agglomeration on the sinterabil-

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ity of yttria-stabilized zirconia powders prepared under different processing conditions.

## 2 EXPERIMENTAL

### 2.1 Powder Preparation and Characterization

Chemical coprecipitation was used to prepare ultrafine  $\text{ZrO}_2(\text{Y}_2\text{O}_3)$  powders. The flowsheet along with the processing conditions are shown in Fig. 1.

The morphologies of primary particles and agglomerates were studied using a transmission electron microscope (TEM) and a scanning electron microscope (SEM), respectively. The BET method was employed to determine the pore diameter and specific pore volume from which the relative density of agglomerates was calculated<sup>[8]</sup>.

### 2.2 Powder Compaction and Sintering

Both as-calcined and ball-milled powders were granulated by isostatic compaction at a pressure of 50 MPa. The granulated powders were then prepressed in a die with double actions at a pressure of 100 MPa, followed by isostatic compaction at a pressure of 260 MPa. The densities of the compacts were measured by their weights and dimensions. The com-

pacts were finally sintered in air at 1460 °C for 4 h. The densities of the sintered samples were measured by the Archimedes method.

## 3 RESULTS AND DISCUSSION

Fig. 2 illustrates the TEM micrographs of the as-calcined powder treated by supersonic dispersion, showing that the primary particle sizes of the powders prepared under different processing conditions are much the same, which range from 20 to 40 nm. Fig. 3 illustrates the SEM micrographs of both as-calcined and ball-milled powders. As can be seen, the particle sizes are much greater than those illustrated in Fig. 2, indicating that the powders are all in the form of agglomerates. The sizes of agglomerates in ball-milled powders are much less than those in as-calcined powders, but still much greater than primary particle sizes.

Table 1 shows the structural characteristics of agglomerates in as-calcined powders. As indicated in the table, the structure of agglomerates in powder ZY1 is the most compact while that in powder ZY2 is the loosest. Table 2 shows the compactability and sinterability of as-calcined and ball-milled powders. For as-calcined powders, the sinterability of the pow-

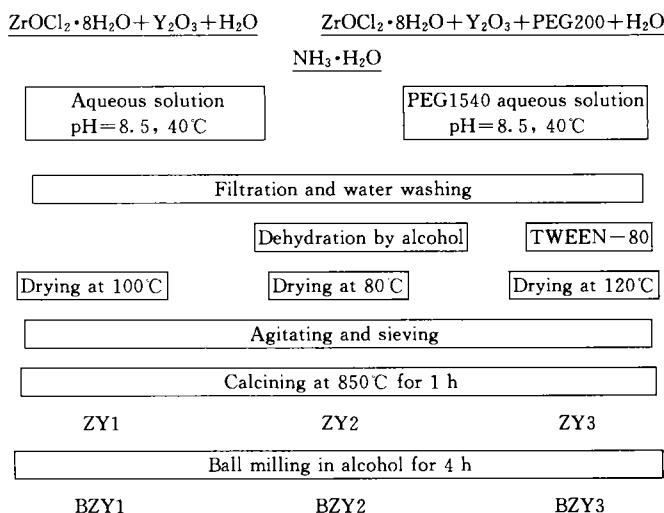


Fig. 1 Flowsheet for preparing ultrafine  $\text{ZrO}_2(\text{Y}_2\text{O}_3)$  powders

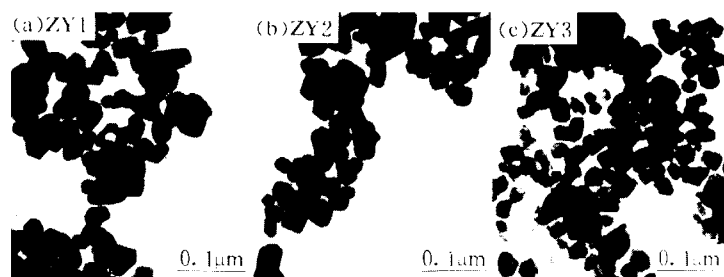


Fig. 2 TEM micrographs of as-calcined powders showing primary particle morphologies

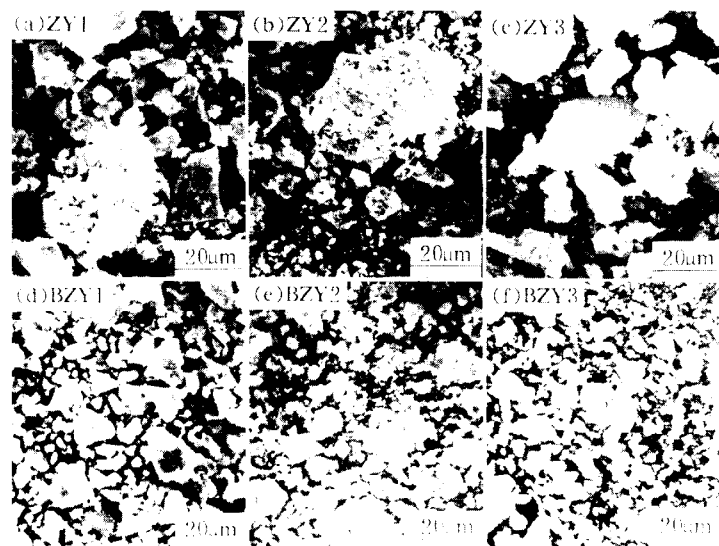


Fig. 3 SEM micrographs of as-calcined and ball-milled powders showing agglomerate morphologies

**Table 1 Structural characteristics of agglomerates in as-calcined powders**

Powder	Mean pore diameter/nm	Specific pore volume/cm <sup>3</sup> •g <sup>-1</sup>	Agglomerate density/%
ZY1	23.49	0.141	53.84
ZY2	29.94	0.207	44.28
ZY3	24.99	0.185	47.06

**Table 2 Sinterability of ZrO<sub>2</sub>(Y<sub>2</sub>O<sub>3</sub>) ultrafine powders**

Powder	Density of compact		Density of sintered sample		Sintering shrinkage
	/g•cm <sup>-3</sup>	/%	/g•cm <sup>-3</sup>	/%	/%
ZY1	1.934	48.90	5.419	89.13	17.91
ZY2	2.934	49.41	5.998	98.66	21.21
ZY3	2.872	47.86	6.043	99.40	21.36
BZY1	3.055	52.58	5.862	96.41	20.00
BZY2	3.114	53.60	6.054	99.57	20.37
BZY3	2.975	51.20	5.993	98.57	21.17

Note: Theoretical densities of 6.08 g/cm<sup>3</sup> and 5.81 g/cm<sup>3</sup> were taken for as-calcined and ball-milled powders, respectively, and theoretical density of 6.08 g/cm<sup>3</sup> was taken for sintered bodies.

der derived from direct drying and calcination of water-washed hydroxide gels is the poorest. Further dehydration by alcohol or treatment by some surfactants can significantly improve the sinterability. By making a comparison between as-calcined and ball-milled powders, it can be drawn that ball-milling appears to be very effective to improve the sinterability of powder ZY1 but has little influence on that of powders ZY2 and ZY3.

If agglomerates are not completely crushed during compaction, differential sintering<sup>[8]</sup> may occur due to the different packing behavior of primary particles in agglomerates and matrix. This indicates that the matrix is still porous when agglomerates are fully densified. Further densification of the sintering sample will be impeded since the fully dense agglomerates become rigid inclusions. Assuming that the sintering sample will no longer densify as soon as agglomerates are sintered to theoretical density, the following equation may be derived<sup>[9]</sup>:

$$D = \frac{D_0}{D_a} \quad (1)$$

where  $D$ ,  $D_0$ , and  $D_a$  are the relative densities of the sintered sample, green compact, and agglomerates, respectively. According to Eq. (1), low agglomerate density and high

compaction pressure are necessary to increase the sintered density. As can be calculated from Tables 1 and 2, the values of  $D_0/D_a$  for powders ZY1 and BZY1 are 0.908 and 0.976, which are quite close to the experimental data of sintered density.

In the case of the density of agglomerates lower than that of matrix, the fully densifying shrinkage of agglomerates will be greater than that of matrix. When matrix is sintered to theoretical density, further shrinking of agglomerates will leave large pores, and further shrinking of the sintering sample will thus almost no longer occur. The sintered density corresponding to this stage can be expressed by<sup>[9]</sup>:

$$D = \frac{D_a - fD_0}{(1-f)D_a} \quad (2)$$

where  $f$  is the fraction of uncrushed agglomerates remaining in the compact. As indicated by Eq. (2), sintered density increases with the decrease of the value of  $f$  and with the increase of the agglomerate density. In general, however, in the case of the density of agglomerates lower than that of the compact, almost complete crushment of agglomerates may be expected. For powders ZY2, ZY3, BZY2, and BZY 3 in which the densities of

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## 5 REACTOR USED IN OPERATION OF CONVERSION<sup>[10]</sup>

It has been proved by enlarged experiments charged 50 Kg concentrate of PbS containing Au that the propeller agitation reactor without baffles is available for the conversion of galena into PbCO<sub>3</sub>. The optimum parameters of the reactor are:  $D/d = 3.5$ ,  $H/C = 7$ , the dip angle of paddle being 45°. Where  $D$  is the diameter of the reactor(m);  $d$  diameter of the paddle of the agitator(m);  $H$  height of the reactor(m);  $C$  distance from the paddle to bottom of the reactor. The conversion efficiency of the reactor is more than 99% and the energy consumption is lower.

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(From page 40) agglomerates are lower than those of the compacts, the sintered densities are quite close to theoretical density. Hence, in order to increase the sintered density, it is necessary to decrease the agglomerate density as much as possible.

## 4 CONCLUSIONS

(1) When chemical coprecipitation is used to prepare ultrafine ZrO<sub>2</sub> (Y<sub>2</sub>O<sub>3</sub>) powders, poor sinterability for the powder derived from direct drying and calcination of water-washed hydroxide gels is observed. Ball-milling is found to be an effective way to improve the sinterability of the powder, and the sintered density is increased from 89% to 96% of theoretical density.

(2) The powder sinterability can be greatly improved by adding some surfactants during the coprecipitation and before drying of hydroxide gels, and the sintered density high-

er than 98% is obtained, which is quite close to that of the powder derived from alcohol-washed gels.

(3) The key to increase the sintered density is to lower the agglomerate density and strength as well as to increase the compaction pressure.

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