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Wet-Milling Effect on the Properties of Ultrafine Yttria-Stabilized Zirconia Powders

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Abstract: Chemical coprecipitation was used to produce ultrafine yttria-stabilized zirconia powders. The effect of wet-milling on the properties of the powders derived from different processing conditions was investigated. It was shown that the agglomerates in the as-calcined powders were mainly crushed into smaller agglomerates during wet-milling while the aggregate and primary particle sizes were less affected. Wet-milling might be an efficient way to increase the specific surface area of hard agglomerated powders but had little influence on that of soft agglomerated powders. The as-calcined powders were composed of about 95% tetragonal phase, the balance being monoclinic phase. After wet-milling in alcohol for 4 h, some 50% of the tetragonal phase was transformed into monoclinic phase, which resulted in a decrease of the crystal size from 22 nm in as-calcined powders to 17 nm in wet-milled powders. It was also shown that wet-milling might be useful for the improvement of the compactability of as-calcined powders and the sinterability of hard agglomerated powders. For those soft agglomerated powders, it was proved to be unnecessary for wet-milling to be used to improve the powder sinterability.

1 INTRODUCTION

Partially stabilized ZrO_2 (PSZ) is receiving a great deal of attention as a ceramic material[1-5] because of its increased fracture toughness and strength compared to cubic stabilized ZrO_2 (CSZ). The martensitic transformation between the tetragonal and monoclinic phases in the vicinity of a crack tip relieves the fracture stress and increases the fracture toughness. Recently, much work has been devoted to tetragonal ZrO_2 polycrystals (TZP) which contain almost 100% of the tetragonal phase. Because of their unique properties, zirconia-based materials are already finding applications as high temperature furnace insulation, hot extrusion and casting dies, pressure nozzles, melting crucibles, and cutting tools. Potential future applications include engine parts, medical prostheses, and electrical materials.

According to Herring's theory,[6] the use of ultrafine powders is a preferred way to increase the sintered density or reduce the sintering temperatures and times. Also, the use of ultrafine powders is of fundamental importance to produce certain high-quality ceramic materials. Recently, it has been widely demonstrated that the state of agglomeration of powders which are usually derived from wet chemical routes has a major influence on the properties of final products. Successful fabrication of ultrafine ceramic powders often requires the elimination of hard agglomerates in the powders. Hard agglomerates are commonly found in ZrO_2 powders which are synthesized by aqueous precipitation.[7-9] Since these precipitation techniques offer convenient routes to high-purity, ultrafine ceramic powders, a variety of methods have been used to avoid the formation of hard agglomerates including hot kerosene synthesis,[10] citrate synthesis,[10] alkoxide synthesis,[10] chloride synthesis followed by alcohol washing,[11] azeotropic distillation,[12] and freeze-drying.[13] All of these techniques have been demonstrated to be effective in avoiding the formation of hard agglomerates.[14-16] Wet-milling of powders in alcohol has also been used to control

Table 1. Definition of the smaller constituents of a ceramic powder derived from wet-chemical routes

Constituent	Definition	Usual size range	Characterization
Crystallite	Coherently diffracting area of lattice	From 1 to 50 nm	X-ray diffraction analysis Transmission electron microscopy
Primary particle	Fully dense particle composed of crystallites	From 1 to 100 nm	BET method Transmission electron microscopy Small-angle X-ray scattering analysis
Aggregate	Hard and less porous particle composed of primary particles connected mutually by solid necks	From 100 to 1000 nm	Transmission electron microscopy Scanning electron microscopy
Agglomerate	Soft or hard and more or less porous cluster of aggregates weakly connected	From 1 to 100 μm	Scanning electron microscopy Granulometric analysis

the state of agglomeration,[17] but the reports on the effect of wet-milling on the properties of powders are very limited.

The present work is based on several coprecipitated ultrafine yttria-stabilized zirconia powders prepared under different processing conditions. Emphasis is placed on the effect of wet-milling on the basic characteristics, compactability and sinterability of these powders. As the definition of the smaller constituents of a ceramic powder is rather confused, the definition shown in Table 1 will be used in the present work. An overlap of the size ranges between crystallites and primary particles may occur because some primary particles may be composed of a single crystallite.

2 EXPERIMENTAL PROCEDURES

2.1 Powder preparation

The powders used in this study were prepared by coprecipitation in aqueous solution. Appropriate quantities of $ZrOCl_2{\cdot}8H_2O$ and Y_2O_3 were dissolved in 4 litres of distilled water to yield 250 g of $ZrO_2(Y_2O_3)$ powder of final composition 2·3 mol% Y_2O_3. This mixture was added dropwise to a continuously stirred NH_4OH solution which was maintained at pH 8·5 and 40°C. Additional NH_4OH solution was used to neutralize the chloride solution to ensure that the pH remained constant during the coprecipitation of Zr and Y hydroxides. The resulting gelatinous precipitate was vacuum filtered and washed with distilled water until chloride ions could no longer be detected in the filtrate. The gel was divided into three parts. The first was dried directly at 100°C (powder A); the second was washed three times with alcohol and then dried at 80°C (powder B); and the third was treated with a surfactant ('Tween' 80) and then dried at 120°C (powder C). After drying, gels A, B, and C were ground to a particle size of < 140 mesh and then calcined at 850°C for 1 h. The powders obtained were denoted as ZY-A, ZY-B and ZY-C, respectively. The calcined powders were wet-milled in alcohol for 4 h to give BZY-A, BZY-B, and BZY-C, respectively.

2.2 Powder characterization

The phase composition of the powders was determined by X-ray diffraction analysis and the crystal size by the X-ray line broadening method. The integral breadth of the line was corrected for instrumental broadening by the Cauchy–Gaussian function.[18] The primary particle size was determined by small-angle X-ray scattering (SAXS) technique[19] and the morphologies of primary particles were studied using a transmission electron microscope (TEM). In order to eliminate the effect of agglomerates, the powders were ultrasonically dispersed in a water–alcohol mixed solution before SAXS and TEM studies. After standing for 24 h, the suspended particles which were regarded as nonagglomerated or primary particles were taken as the samples for SAXS and TEM studies. The specific surface area of the powders was determined by the BET method and the equivalent BET particle size was calculated using the equation:

$$d = \frac{6}{\rho S} \tag{1}$$

where d is the particle diameter, ρ is the theoretical density of the powder material and S is the specific surface area of the powder.

The morphology of the agglomerates as well as their microstructure were studied using a scanning electron microscope (SEM). The cumulative size distribution of the agglomerates was determined by ultrasonically dispersing the powders in alcohol followed by centrifugal sedimentation. The pore

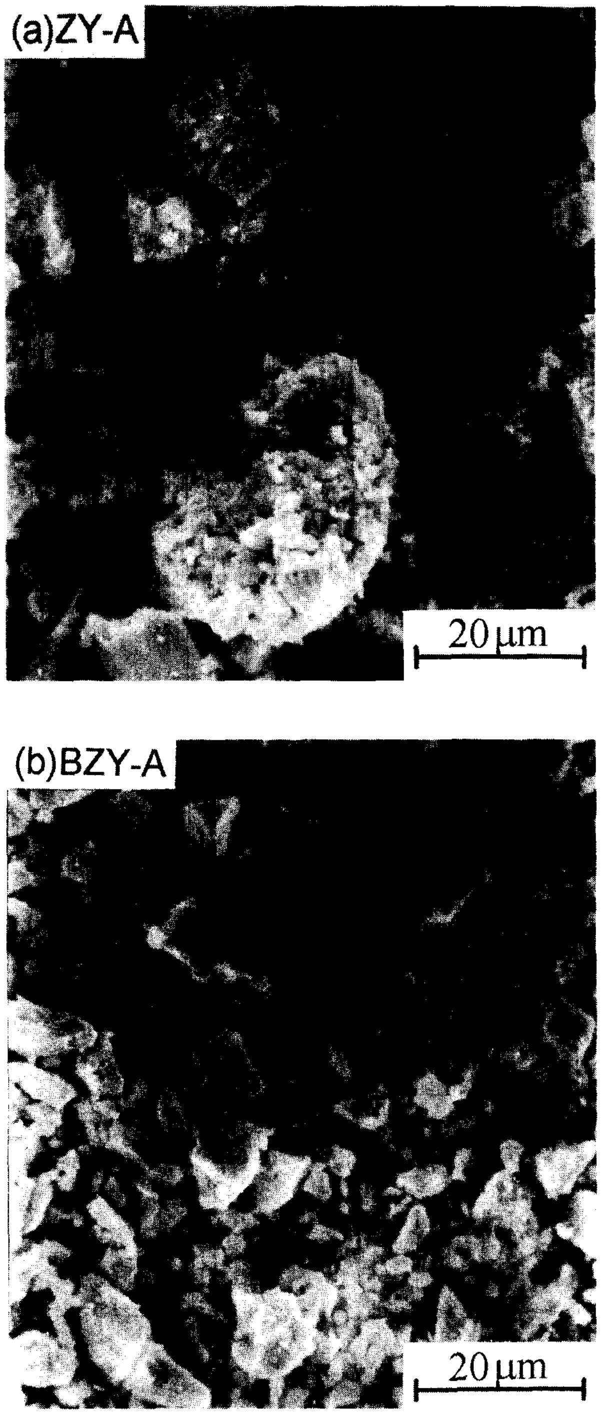

Fig. 1. SEM micrographs showing the morphologies of agglomerates in powders ZY-A and BZY-A.

size distribution in the loose powders was measured using a mercury porosimeter. The surface tension of mercury and the contact angle were taken as 0·48 N/m and 141·3°, respectively.

2.3 Compaction and sintering

Both as-calcined and wet-milled powders were granulated by isostatic compaction at a pressure of 50 MPa after crushing to < 140 mesh. The granulated powders were then prepressed in a die with double action at a pressure of 100 MPa followed by isostatic compaction at a pressure of 260 MPa. The green densities of the compacts were measured by their weights and green dimensions. The compacts were finally sintered in air at 1460°C for 4 h. The fired densities of the sintered samples were measured by the Archimedes method.

3 RESULTS AND DISCUSSION

3.1 Effect of wet-milling on powder characteristics

Figure 1 illustrates the SEM micrographs of the agglomerates in powders ZY-A and BZY-A, showing that the agglomerates in powder ZY-A are crushed into smaller ones after wet-milling, but their morphologies are quite similar, characterized by a rather wide size distribution of irregularly shaped features. When the agglomerates are viewed at higher magnification as illustrated in Fig. 2, it can be clearly seen that the agglomerates in each powder seem to be composed of several smaller agglomerates which are further composed of very fine and uniform aggregates with a particle size range of 0·1–0·3 μm in diameter. Similar morphologies and microstructure were observed for the agglomerates in powders ZY-B, BZY-B, and ZY-C and BZY-C. Figure 3 shows the cumulative size distributions of the agglomerates in as-calcined and wet-milled powders. Compared with the powder morphologies shown in Fig. 1, the agglomerate size in as-calcined powder ZY-A is obviously smaller than that shown in Fig. 1(a), while that in wet-milled powder BZY-A is closer to that shown in Fig. 1(b). As mentioned above, the powders were dispersed by ultrasonic treatment before the measurement of cumulative size distribution of agglomerates and it can be assumed that after ultrasonic treatment, soft agglomerates will be broken into several smaller agglomerates which are expected to be harder than the original ones. Therefore, it may be inferred that the agglomerates illustrated in Fig. 1(a) can be regarded as soft agglomerates composed of several smaller and weakly connected hard agglomerates which are further composed of aggregates. Wet-milling seems not to be effective in decreasing the sizes of these smaller agglomerates, which may be attributed either to the strength or to the small size of the smaller agglomerates.

The pore size distributions in the loose as-calcined powders are shown in Fig. 4. The bimodal nature of the curves indicates two different pore populations — the large pores among the agglomerates and the smaller pores within the agglomerates. Therefore, the pore volume within the agglomerates can

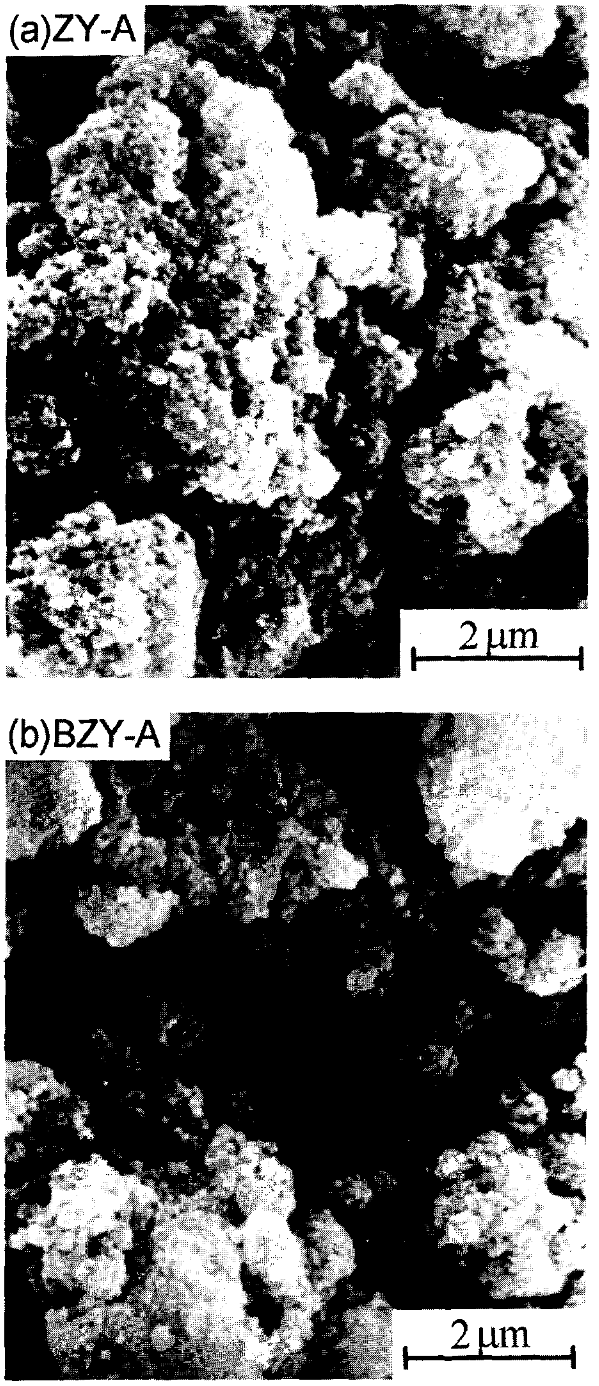

Fig. 2. SEM micrographs showing the microstructure of agglomerates in powders ZY-A and BZY-A at higher magnification.

be obtained so that the relative density of the agglomerates may be calculated by:

$$D_a = \frac{\frac{fm}{\rho}}{\frac{fm}{\rho} + V_a} = \frac{f}{f + \rho(V_a/m)} \qquad (2)$$

where D_a is the relative density of the agglomerates, m is the mass of the powder, f is the mass fraction of the agglomerates in the powder, V_a is the pore volume within the agglomerates, and ρ has been

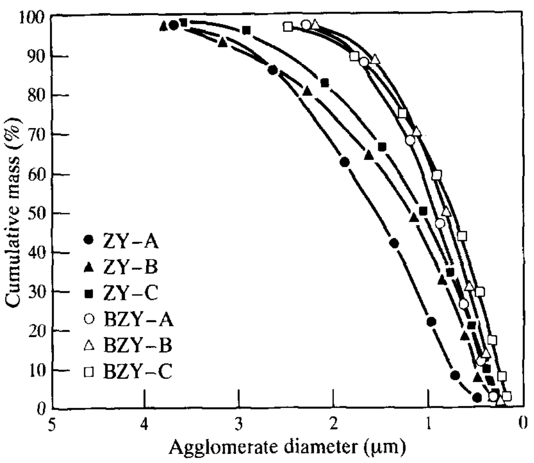

Fig. 3. Cumulative size distributions of agglomerates in as-calcined and wet-milled powders.

Table 2. Agglomerate structure of as-calcined powders

Powder	Mean pore dia. (nm)	Pore volume (cm^3g^{-1})	Agglomerate density (%)
ZY-A	23·49	0·141	53·84
ZY-B	29·94	0·207	44·28
ZY-C	24·99	0·185	47·06

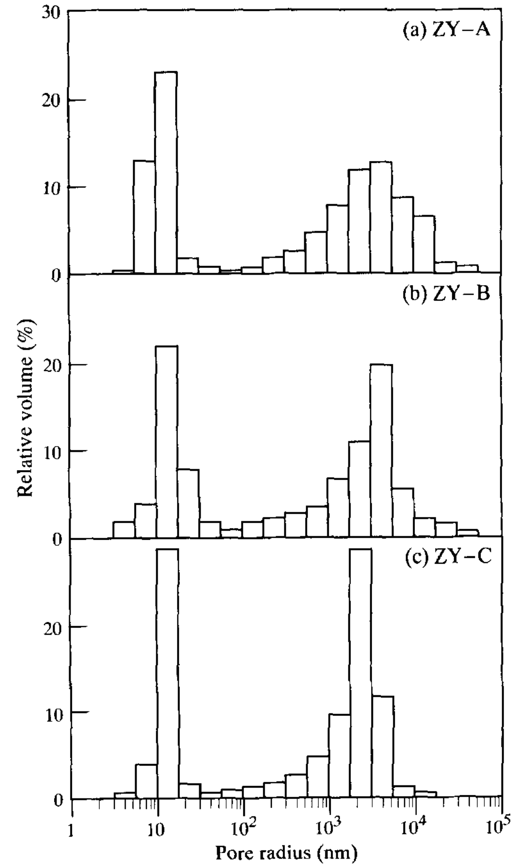

Fig. 4. Pore size distributions in loosely packed as-calcined powders.

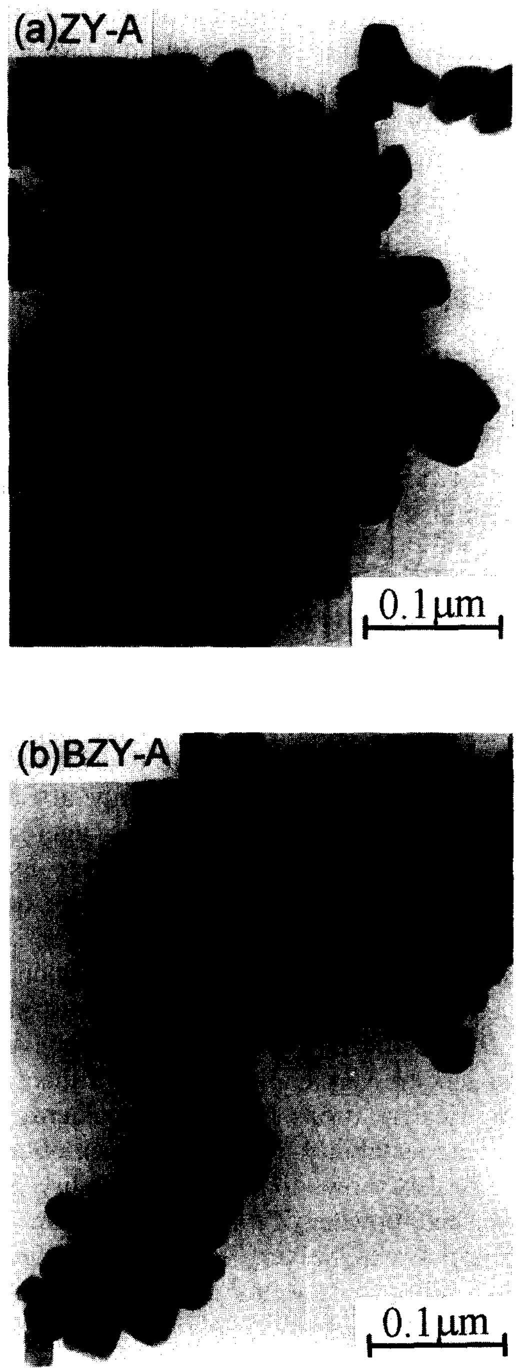

Fig. 5. TEM micrographs of primary particles in powders ZY-A and BZY-A.

defined above. As shown in Figs 1 and 3, the as-calcined powders can be regarded as being completely agglomerated. Therefore, the value of *f* in eqn (2) can be approximately taken as unity. The theoretical densities of the powders can be calculated from their phase compositions which will be shown later. The calculated results of the agglomerate densities are shown in Table 2. It can be deduced from the table that the structure of agglomerates in water-washed powder ZY-A is compact, while that in alcohol-washed powder ZY-B and in surfactant-treated powder ZY-C is more porous.

Figure 5 shows the TEM morphologies of primary particles in powders ZY-A and BZY-A. It can be seen from the figure that the primary particle morphologies and sizes of the two powders are much the same. Figure 6 shows the primary particle size distributions of both as-calcined and wet-milled powders determined by SAXS. As can be seen, wet-milling seems to have little influence on the primary particle sizes and size distributions of the as-calcined powders prepared under different processing conditions.

Some characteristics of both as-calcined and wet-milled powders are shown in Table 3. As can be seen from the table, the as-calcined powders are mainly composed of the tetragonal phase. After wet-milling, some 50% of the tetragonal phase in each as-calcined powder is transformed into the monoclinic phase. Based on the phase compositions, the theoretical density values of 6·08 g/cm^3 and 5·81 g/cm^3 for as-calcined and wet-milled powders can be calculated. It is of interest to note that the primary particle sizes of the as-calcined powders are much the same while their specific surface areas or the equivalent BET particle sizes are evidently different from one another. Considering the fact that the specific surface area of an agglomerated powder in which the primary particles are connected mutually by solid necks is

Table 3. Characteristics of as-calcined and wet-milled powders

Powder	Phase composition (%)		BET specific surface area (m^{2}g^{-1})	BET equivalent particle dia. (nm)	Average crystal dia. (nm)	Average primary particle dia.[c] (nm)
	t-ZrO$_2$[a]	m-ZrO$_2$[b]				
ZY-A	96·3	3·7	16·16	61·1	22·5	30·8
ZY-B	96·0	4·0	26·29	37·5	21·8	30·5
ZY-C	94·9	5·1	31·82	31·0	20·9	28·2
BZY-A	48·0	52·0	28·07	36·8	16·6	29·8
BZY-B	52·1	47·9	29·70	35·5	17·7	29·7
BZY-C	44·6	55·4	35·80	28·8	16·4	27·4

[a] t = tetragonal.
[b] m = monoclinic.
[c] Determined by small-angle X-ray scattering technique.

Table 4. Densities of compacts and sintered samples of as-calcined and wet-milled powders

Powder	Pressed density[a] (%)	Sintered density[b] (%)
ZY-A	48·90	89·13
ZY-B	49·41	98·66
ZY-C	47·86	99·40
BZY-A	52·58	96·41
BZY-B	53·60	99·57
BZY-C	51·20	98·57

[a] Pressed isostatically under 260 MPa.
[b] Sintered at 1460°C for 4 h.

closely related to the state of agglomeration of the powder, it can be understood that the higher value of the specific surface area of a powder implies a lower degree of agglomeration of the powder to some extent when the primary particle size is fixed.

Making a comparison between as-calcined and wet-milled powders, it can be found that the specific surface area of powder BZY-A is evidently larger than that of powder ZY-A, while those of powders BZY-B and BZY-C are quite close to those of powders ZY-B and ZY-C. In addition, the primary particle sizes of the powders seems not to be obviously changed after wet-milling. These results indicate that the solid necks between mutually connected primary particles within the agglomerates in powder ZY-A occupy a lot of area, while those in powders ZY-B and ZY-C do little. Since the strength of agglomerates mainly depends on the nature of solid necks between primary particles, it may be a useful way to judge the strength of the agglomerates by making a comparison between the specific surface areas of the powders before and after wet-milling.

It is of interest to note that the crystal sizes in wet-milled powders are evidently smaller than those in as-calcined powders. From the phase compositions of the as-calcined and wet-milled powders, the decrease of crystal sizes of the as-calcined powders during wet-milling should be due to the transformation of the tetragonal to monoclinic phase.

3.2 Effect of wet-milling on powder compactability and sinterability

The effects of wet-milling on the compactability and sinterability of as-calcined and wet-milled powders are shown in Table 4. By making a comparison between the pressed densities of as-calcined and wet-milled powders, it can be shown that wet-milling seems to be useful in improving the compactability of the powders prepared under different processing conditions. As discussed above, the main changes of the powder features after wet-milling are the decrease of agglomerate and crystal sizes as well as the transformation between tetragonal and monoclinic phases. Since the densification of powders during compaction is mainly attributed to the rearrangement of agglomerates, aggregates, and primary particles at the pressures usually employed, the role played by crystal size during this stage of densification is expected to be small. The transformation and the decrease of agglomerate size might play a certain role in the densification. As the factors affecting the compaction behavior of real powders are very complicated, both theoretical and empirical relations between agglomerate size and the compactability have not yet been obtained.

Table 4 also shows that the sinterability of the water-washed powder ZY-A is very poor. Wet-milling appears to be very effective in improving its sinterability but seems to be ineffective in improving the sinterability of soft agglomerated

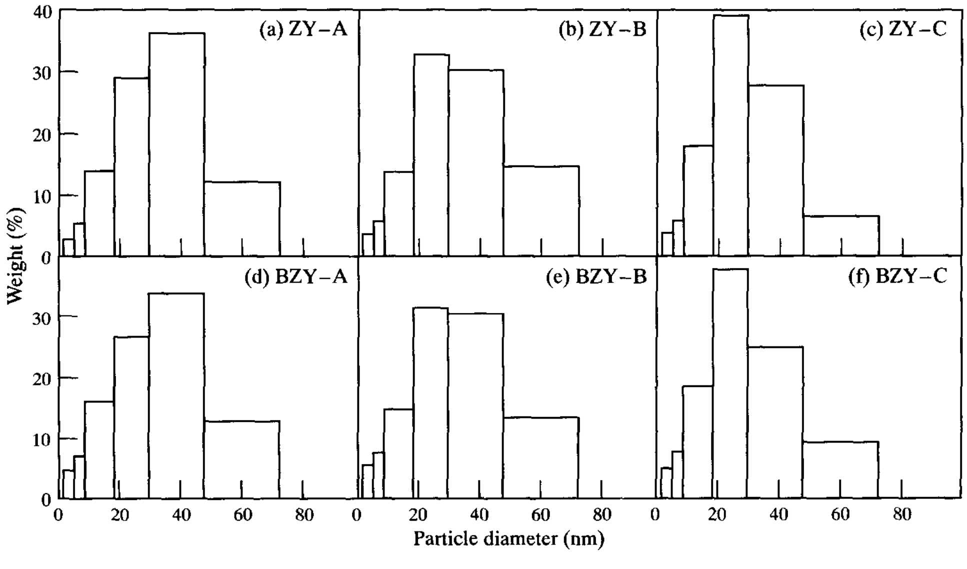

Fig. 6. Primary particle size distributions of as-calcined and wet-milled powders measured by small-angle X-ray scattering analysis.

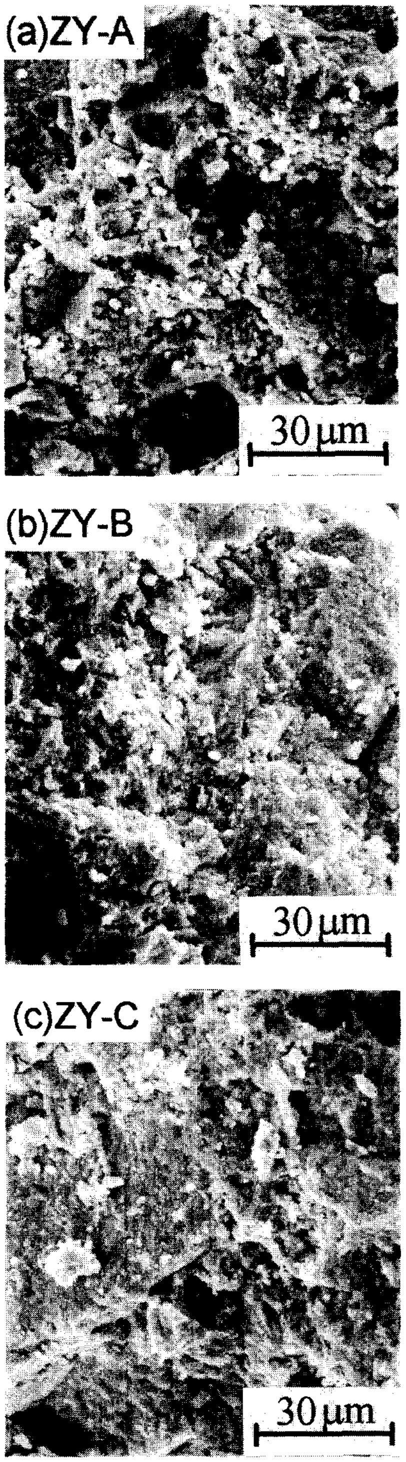

Fig. 7. SEM micrographs showing the microstructure of the compacts of as-calcined powders.

powders ZY-B and ZY-C. Figure 7 illustrates the SEM microstructure of the compacts of as-calcined powders, showing that there are some large pores among the uncrushed agglomerates in the compact of water-washed powder ZY-A, while the pore sizes in the compacts of alcohol-washed powder ZY-B and surfactant-treated powder ZY-C are very uniform. This suggests that the agglomerates in the latter two powders were almost completely crushed during compaction. If some agglomerates are not crushed during compaction, it is reasonable to expect that the larger the agglomerate size in a powder, the larger will be the size of the uncrushed agglomerates remaining in the compact. It may also be expected that the harder the agglomerates, the larger will be the size of the uncrushed agglomerates in the compact. In the case of water-washed powder BZY-A, as the agglomerate size decreased after wet-milling, the sizes of pores among the uncrushed agglomerates in the compact are expected to be less than those in the compact of the as-calcined powder, through which the sinterability can be improved. Furthermore, Lange[20] has demonstrated that the coordination number of interagglomerate pores will decrease with decreasing agglomerate size without changing their volume contribution to the total void volume, through which the sinterability of the powders can also be improved. In the case of powders BZY-B and BZY-C, since the agglomerates were almost completely crushed, the decrease of the agglomerate size after wet-milling will be of little importance both in decreasing the pore sizes and in decreasing the coordination number of interagglomerate pores.

4 CONCLUSIONS

Ultrafine yttria-stabilized zirconia powders were produced by chemical coprecipitation under different processing conditions. The critical operation is the method of removing water from coprecipitates before drying. Direct calcination of water-washed gels resulted in a powder composed of hard agglomerates which had a compact structure. The calcination of water-washed gels after alcohol dehydration or surfactant treatment gave a powder composed of more porous agglomerates. It was found that the agglomerates in as-calcined powders were crushed into smaller agglomerates during wet-milling but the aggregate and primary particle sizes were little affected. Wet-milling might be an efficient way to increase the specific surface area of hard agglomerated powders but might be useless to increase that of soft agglomerated powders. The as-calcined powders were composed of 95% or more tetragonal phase, the balance being monoclinic phase. After wet-milling in alcohol for 4 h, about 50% of the tetragonal phase in each as-calcined powder was transformed into monoclinic phase, which resulted in a decrease of the average crystal size from 22 nm in as-calcinated powders to 17 nm in wet-milled powders. The present work also found that wet-milling might be useful in improving the compactability of as-calcined powders and the sinterability of hard agglomerated powders. For those soft agglomerated powders, wet-milling proved unnecessary to improve the powder sinterability.

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