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Characteristics of the Pore Structures in the Compacts of Ultrafine Zirconia Powder

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Compaction behavior of two batches of yttria-stabilized zirconia powders containing different kinds of agglomerates were investigated with the help of pore size distribution measurements for powders and compacts. The pore structure changes during the powder compaction show that the weakest agglomerates obtained with the total dewatering by ethyl alcohol are eliminated in compaction at not higher than 100 MPa and are independent of calcination temperature. Agglomerates in untreated powder with alcohol are strong and cannot be broken at even 500 MPa. Different compaction behaviors of agglomerates are thought to be due to the whole different process taking place during drying and decomposition of the untreated and treated powders. © 1991 Academic Press, Inc.

Introduction

Powders, especially fine powders, with the same particle size can show very different sintering behavior (*1–3*), which is due to the different properties of the agglomerates in the powders used. Furthermore, agglomerates with the same size, shape, or content in powders differently processed would behave rather differently in compaction and sintering, i.e., the properties of the agglomerates, besides their geometric properties, are process-dependent. The agglomerate behaviors during compaction of the superfine yttria-stabilized zirconia powder obtained with the different processes are described, and the reasons for the different behaviors are discussed with the relation to the powder processing history.

Experiments

Powders of 7 mol% Y_2O_3-stabilized ZrO_2 were prepared by a coprecipitation and spray-drying method as described in detail elsewhere (*4, 5*). Spray drying was conducted in a mini-spray dryer (Brinkman/Buchi model 190, Westbury, NY). Two batches of powders were obtained with different washing processes: powder *A* was prepared by washing the coprecipitate with ethyl alcohol thoroughly to remove the water in the coprecipitated cake, and powder *W* was prepared by only water washing (untreated with ethyl alcohol) of the coprecipitates before spray drying. Washing with alcohol of the coprecipitates may result in the improved sinterability of the powder as reported by Haberko (*6*) 10 years ago.

The spray-dried powders were calcined at various temperatures from 420 to 1000°C for

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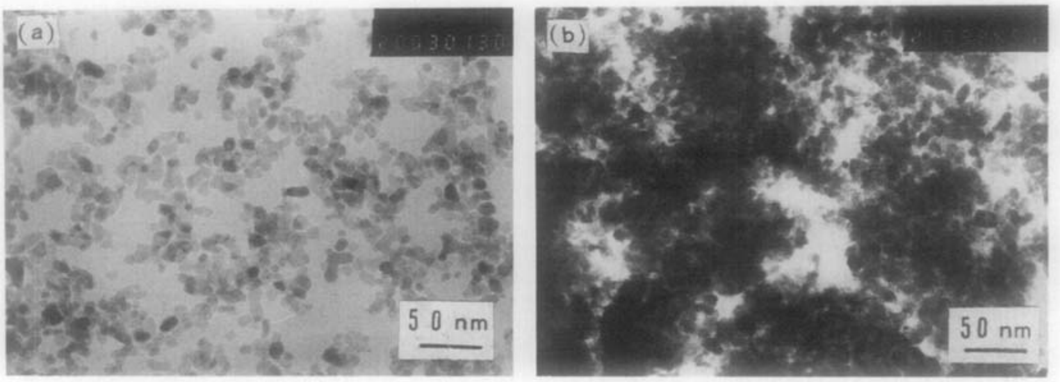

FIG. 1. Particle morphologies (TEM's) of (a) powder *A* and (b) powder *W* (600°C).

25 min, followed by compaction with die-pressing at 100 to 500 MPa. This gave disk samples of 2 cm in diameter and about 3 mm in thickness. The powders and the compacts were analyzed of their pore size (in diameter) distributions with Hg-porosimetry (Micromeritics, Model 9200) in the pore size range from 300 μm to 30 Å. Primary particle morphologies were observed with TEM (transmission electron microscopy, JEM-200CX, JEOL) after ultrasonic treatment, and the agglomerates were observed with SEM (JCXA-733, JEOL) without ultrasonic treatment.

Results

1. Particle Morphologies and Pore Size Distributions of Powders

Particle morphologies (TEM's) of the powders are shown in Fig. 1(a) (powder *A*) and Fig. 1(b) (powder *W*). Powder *A* shows particles do not strongly agglomerate, i.e., the primary particles are not connected with each other obviously; but powder *W* shows the extensive formation of strong agglomerates between the primary particles, as indicated in Fig. 1(a) and 1(b), respectively.

Figure 2 illustrates the SEM micrograph of the spray-dried powder calcined at 600°C, showing basically spherical agglomerates formed in spray drying, with their sizes of about several micrometers. It can also be seen that the most primary particles are agglomerated.

Figure 3 shows the pore size distributions of powder *A* after calcination at different temperatures. Three kinds of pores can be distinguished from the figure, as discussed elsewhere (*4, 7*): (a) primary pores (inter-primary particles), (b) secondary pores (inter-agglomerates), and (c) largest tertiary pores between the secondary agglomerates,

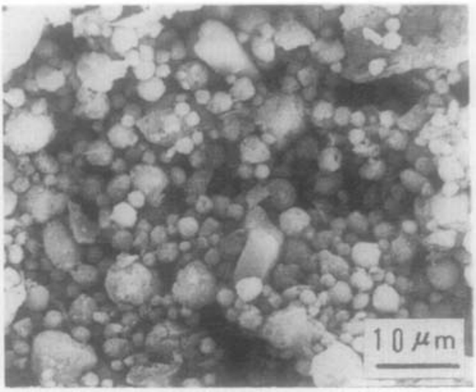

FIG. 2. SEM micrograph of the agglomerates in co-precipitated and spray-dried powder calcined at 600°C.

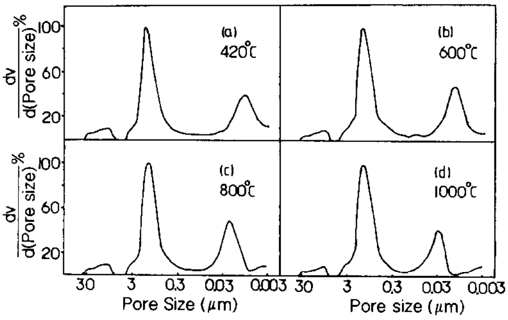

FIG. 3. Volume distributions of the pore size in powder *A* calcined at (a) 420°C, (b) 600°C, (c) 800°C, and (d) 1000°C.

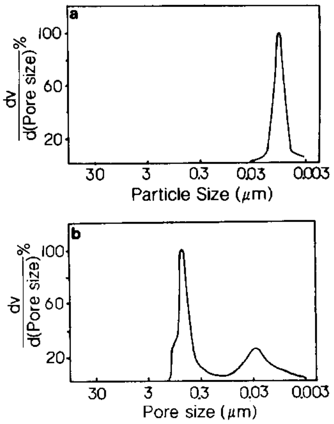

FIG. 4. Pore size distributions of the compacts of (a) powder *A* and (b) powder *W* after calcination at 600°C and compaction at 100 MPa.

which are formed by the agglomeration of agglomerates, with their size ranges of 0.003–0.1 μm, 0.1–5 μm, and 5–35 μm, respectively. The content of the tertiary pores is much less than that of the two others, so the secondary agglomeration effect of agglomerates is relatively unimportant. The pore size distributions of powder *W* are similar to powder *A* with those three kinds of pores, as the pore size distribution is only affected by the particle and agglomerate sizes, their size distributions, and the packing conditions, but not by the agglomerate strength.

2. *Powder Compaction Behavior*

The properties of the pores (e.g., sizes, size distributions) is an expression of the particle properties and their packing conditions to a certain extent. In the ideal compacts of monosized spheres, the size of the openings, measured by Hg-porosimetry, through which mercury is intruded into the pores (cavities), are 0.414 and 0.523 times the sphere diameter for the inter-three and inter-four sphere openings (in one plane), so the pore size distributions (opening size, in fact) by Hg-porosimetry stand for the particle size distributions to a certain extent in the powder tested. The elimination of the pores stands for the fragmentation or elimination of the correspondent particles by which the pores are formed in compaction.

Though powder *A* and powder *W* have the similar pore size distributions with different primary particle morphologies (Fig. 1), the two batches of powders behaved differently in compaction, as illustrated in

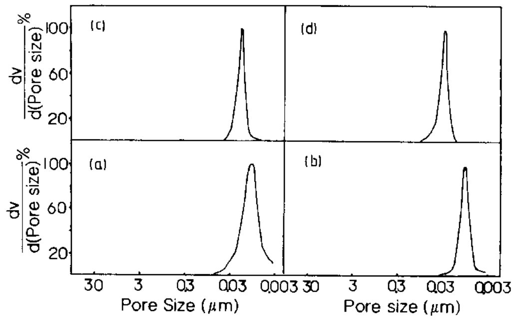

FIG. 5. Pore size distributions of powder *A* calcined at (a) 420°C, (b) 600°C, (c) 800°C, and (d) 1000°C, after compaction at 100 MPa.

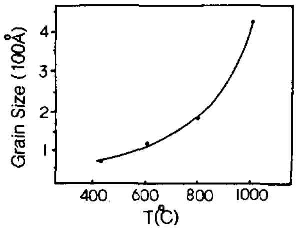

FIG. 6. The temperature dependence of the primary particle size of powder *A* by X-ray diffraction-line broadening technique.

Fig. 4(a) and 4(b). Figure 4(a) is the pore size distribution of powder *A* after compaction at 100 MPa; the secondary pores and the tertiary pores were eliminated, as can be seen in the figure, and it is reasoned that the secondary agglomerates and the agglomerates were fragmented during the compaction. The secondary agglomerates of the untreated powder were also eliminated by compaction, but the agglomerates in the powder were almost unaffected (with only a little decrease of the pore size and its volume) at the same pressure with powder *A*, as shown in Fig. 4(b).

3. *Temperature and Pressure Dependence of the Compaction Behavior*

The dried powders were calcined from 420 to 1000°C. The pore size distributions of powder *A* after compaction are shown in Fig. 5. Calcination temperature does not affect the pore size distribution of the compacts much and does not influence the fragmentation of the agglomerates in compaction. The strength of the agglomerates are temperature-independent basically, though the calcination temperature does affect the sizes of primary particles and primary pores as shown in Figs. 6 and 7.

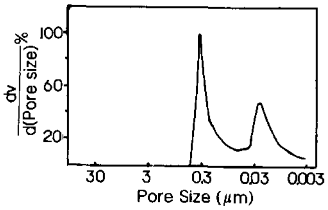

FIG. 8. Pore size distribution of the compact at 500 MPa of powder *W*.

The secondary pores of powder *W* were not eliminated by compaction at 100 MPa, as shown in Fig. 3. The increase of the compaction pressure up to 500 MPa did not give rise to any major changes of the pore size distributions and did not affect the agglomeration behavior, as illustrated in Fig. 8 and Table I. The change of the pore volume and size stand for a partial breakdown or the deformation of the porous agglomerates under pressure.

The compaction behaviors of powder *A* and powder *W* are related to the essential difference in the properties, especially the strength, of the agglomerates in them.

Discussion

The different treatments of the coprecipitates by washing result in two batches of powders with totally different agglomerate

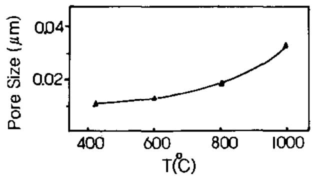

FIG. 7. The temperature dependence of the primary pore size in powder *A*.

TABLE I

SECONDARY PORE VOLUME (ml/g) AND ITS SIZE (μm) IN POWDER *W* AND IN ITS COMPACT

Pressure (MPa)	0	100	500
Pore volume	0.604	0.175	0.082
Pore size	1.38	0.513	0.230

properties. The treatment with alcohol for the coprecipitates means the subtraction of water and/or non-bridging OH^-s with ROH and/or the -OR group. According to the reports by S. L. Jones and C. J. Norman (*8*), alcohol washing can affect the most components in the zirconium hydroxide molecules, including free water, chemically coordinated water, and non-bridged OH^-s. The formation of agglomerates is the result of an oxo-bridging effect between the non-bridging OH^-s among the zirconium hydroxide molecules during heat treatment (drying and calcination). The subtraction of water and non-bridged OH^-s with ROH and the -OR group results in the alternation of the molecular formula and the change of the drying and the decomposition processes. The evaporation of the free water and the coordinated water is replaced by the evaporation of alcohol, which has much lower surface tension than water has, and the oxo-bridging among zirconium hydroxide molecules of the non-bridging OH^-s is replaced by the decomposition and/or burning out of -OR groups. Thus, the strong agglomeration caused by the oxo-bridging between non-bridging OH^-s among the zirconium hydroxide molecules is greatly lessened. The spherical agglomerates in the spray-drying of powder *A* are rather weak and can be broken at relatively low pressure, as the drying and the decomposition process is altered by the alcohol treatment for the coprecipitates. The above discussion also implies that the agglomeration effect of zirconia powders prepared by the coprecipitation method takes place in the transformation process from hydroxide to oxide.

Conclusions

1. Agglomerates of the alcohol treated powder are weak and can be eliminated in compaction at not higher than 100 MPa, and this behavior is insensitive to calcination temperatures.
2. Hard agglomerates form in the untreated powder with alcohol, which cannot be effectively eliminated at a pressure as higher as 500 MPa.
3. Formation of hard agglomerates takes place during the transformation of hydroxide to oxide, in which the bonding (oxo-bridging) between non-bridging OH^-s among zirconium hydroxide molecules plays the most decisive role.
4. Alcohol replacement of ROH and -OR groups for water and non-bridging OH^-s eliminates the basis of the formation of hard agglomerates.

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