

# Microstructure Characteristics of Ultra-fine $ZrO_2$ - $Y_2O_3$ Ceramic Powders\*

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## Abstract

Ytria-doped zirconia powders with an extremely small crystallite size (8 nm) and a narrow size distribution have been prepared by gel precipitation methods. Precipitation of an alkoxide solution in water ("alkoxide" synthesis) results in weaker agglomerates when compared with a precipitation of a metal chloride solution in ammonia ("chloride" synthesis). Both types of agglomerate are fractured during isostatic compaction. The "alkoxide" agglomerates consist of strong small aggregates (15-20 nm) while within the "chloride" agglomerates no, or only a few, aggregates are present.

## 1. Introduction

Ultra-fine and homogeneous zirconia-yttria powders are of importance for the preparation of tough tetragonal zirconia or for cubic zirconia in electronic devices. By means of wet-chemical preparation of ceramic powders very small crystallites can be obtained with a high degree of homogeneity and improved sinterability. Those very fine-grained powders are very difficult to obtain as a really monodispersed powder. They consist of preferably loosely bound aggregates and/or agglomerates [1-6]. These crystallite "clusters" determine for example the powder flow, packing and sintering behaviour of the material [1, 2]. Several definitions are found in the literature for aggregates and agglomerates in ceramic powders. The definition used in this paper has been formulated by Niesz *et al.* [3] whereby an aggregate is a particle composed of crystallites held together by neck areas which are formed by diffusion. An agglomerate is defined as a particle composed of aggregates (or crystallites) which are held together by relatively weak (van der Waals,

capillary) attractive forces. During the wet-chemical synthesis clusters of primary crystallites are essentially formed in the early stages of the preparative method and can be transformed to aggregates or agglomerates during thermal treatments such as drying and calcining [7]. If the agglomerates are too strong to collapse during compaction the pores within the compact can be much larger than the crystallites. Those pores only disappear during sintering at extremely high temperatures or they do not disappear and may even grow [1, 8]. In this paper the preparation of weakly agglomerated ultra-fine-grained zirconia-yttria ceramic powders is described. These powders are the starting materials for fine-grained cubic zirconia (grain size  $0.3 \mu\text{m}$ ) for use as an oxygen ion conducting material [9]. Dense yttria-doped tetragonal zirconia ceramics (Y-TZP) made from these powders can have a grain size as low as  $0.1 \mu\text{m}$  [10].

## 2. Experimental procedure

The zirconia-yttria powders were prepared by two different hydrous-gel precipitation techniques. Both used the hydrolysis of a dilute Zr-Y precursor solution in an excess of hydrolysing agent. In one method (the "alkoxide" method) freshly prepared Zr-t-amyl oxide and Y-isopropoxide were used. A very dilute (0.2 M) benzene solution of these alkoxides was added slowly to a large excess of water (molar ratio  $H_2O$ :metal = 250). The hydrolysis was performed in a dispersion turbine as described in ref. 4. After hydrolysis, the gel was washed three times with water in order to remove organic solvents. The gel was subsequently washed three times with ethanol for removal of the free water within the gel. All washing steps were performed with large amounts of washing agent (gel concentration of about 0.1 M) using a high-energy disc turbine [4].

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The precursors for the second method consisted of commercial  $ZrCl_4$  (Merck) and  $YCl_3$  (Cerac) which were diluted in HCl (0.4 M) (the "chloride" method). This solution was added to an excess of 25%  $NH_4OH$ . During hydrolysis the pH remained at 11 or more. Hydrolysis and washing of the resulting gel were performed in the same reactor that was used for the alkoxide method. Water washing of the chloride-derived gel had to be done very thoroughly in order to remove the chlorides from the solution. For that reason the gel was washed several (about 8) times with a gradually decreasing amount of ammonia in aqueous solution. Subsequently the gel was washed three times with ethanol to remove free water.

Both gels ("alkoxide" and "chloride"-derived) were dried in air for 15 h (120°C) and calcined at 550 °C for 2 h. After drying and calcining the powders were dry milled in plastic containers using teflon balls.

The overall composition was determined by X-ray fluorescence spectrometry. Crystallite sizes of the calcined powders were determined by means of X-ray line broadening measurements using a Philips X-ray diffractometer PW 1710 with Cu  $K_\alpha$  radiation after corrections for instrumental broadening and  $K_\alpha$  splitting were applied. Specific surface areas of the powders were determined by the Brunauer-Emmett-Teller (BET) method as described by Bosch and Peppelenbos [11].

Powder compaction behaviour was investigated by measuring the compact density as a function of the isostatic pressure in the range 4–500 MPa. Overall densities were measured using the Archimedes technique (in mercury). The pore size distribution within the compact was determined by  $N_2$  desorption measurements at liquid nitrogen temperature for pores smaller than 15 nm while for larger pores mercury intrusion porosimetry was used.

### 3. Results and discussion

Zirconia powders with different amounts of yttria could be prepared by means of both precipitation methods. The powder characteristics (compaction behaviour, etc.) were thoroughly studied for zirconia doped with 3 or 9 mol.%  $Y_2O_3$ . The crystal structure is 100% tetragonal and 100% cubic respectively as determined by X-ray diffraction.

The main microstructure characteristics are given in Table 1. The powder characteristics given in Table 1 are independent of the amount of added yttria. A difference in microstructure is, however, observed between the alkoxide- and chloride-derived powders. The crystallite sizes as measured by X-ray line broadening were verified by means of transmission electron microscopy and are shown in Fig. 1. From the BET surface areas a crystallite size can also be calculated if spherical crystallites are assumed. The equivalent BET particle sizes are, respectively, 10 nm and 8 nm for the alkoxide- and chloride-derived powders. For alkoxide powders the crystallite size calculated by the BET surface area is clearly larger if compared with the size determined by X-ray line broadening (Table 1). This difference is probably due to the fact that the "alkoxide" crystallite surface cannot be covered completely by argon during BET measurements. This is an indication that alkoxide powders are more (or more strongly) aggregated than chloride powders as will be discussed later.

The development of microstructures during the compaction process was studied by density measurements and nitrogen-desorption or mercury intrusion techniques. The relative density of

**TABLE 1** Microstructure characteristics of ceramic powders prepared by the hydrolysis of metal alkoxides or metal chlorides

Preparative method	Crystallite size (nm)	$S_{BET}$ ( $m^2 g^{-1}$ )	Agglomerate strength (MPa)	Agglomerate density (relative %)
Alkoxide	8	101	42.5	22
Chloride	8	125	80	30

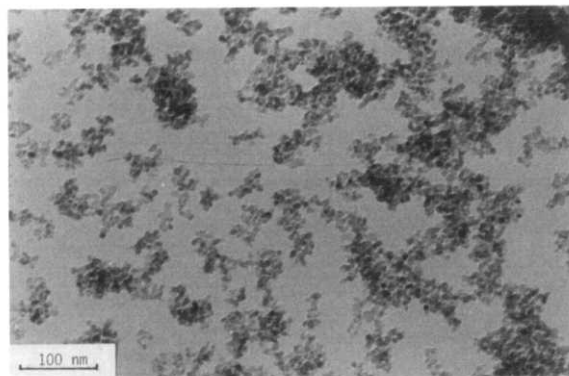


Fig. 1. Transmission electron micrograph of a calcined "chloride" powder.

the powder compacts as a function of the logarithm of the applied isostatic pressure is shown in Fig. 2. In this way the compaction data of both types of powder can be fitted into two linear portions with a break point at pressure  $P_j$ . The (small) densification in the low pressure range can be ascribed to a rearrangement of the agglomerates. Below  $P_j$  the porosity and size of the agglomerates remain the same which means that no change in the internal agglomerate structure is expected [4, 6]. Here, only the pores between the agglomerates disappear. The agglomerate density as given in Table 1 is determined by measuring the pore volume of those pores which do not change in size and volume below  $P_j$  [6]. The linear relation between the logarithm of the compaction pressure vs. relative density indicates an identical compaction mechanism within the pressure range considered. In the high pressure range the density  $\rho$  and the pressure  $P$  can be described by the empirical relation [2, 3]

$$\rho - \rho_j = m \ln(P/P_j)$$

Here,  $P_j$  and  $\rho_j$  are the pressure and density at the point of yielding and  $m$  is an empirical constant. The yield pressure  $P_j$  is a parameter which depends on the strength of the agglomerates. At compaction pressures above  $P_j$  the agglomerates with strength  $P_j$  are fragmented. In this pressure range the pores within the agglomerates diminish, while a rearrangement of aggregates and/or crystallites takes place. The lower agglomerate strength of the alkoxide powder when compared with the chloride powder could be a result of the lower agglomerate density (Table 1) [7]. Both

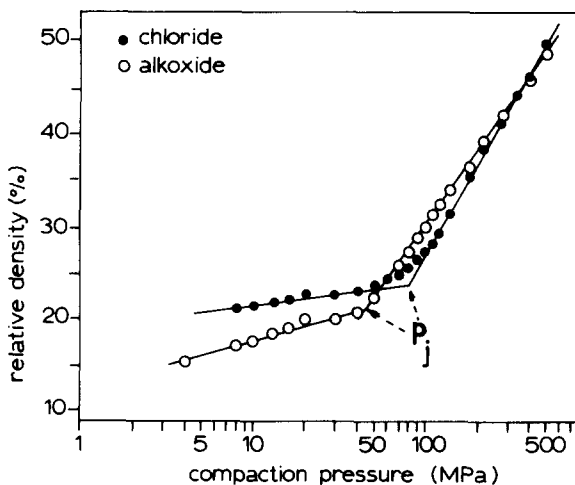


Fig. 2. Densification behaviour of the  $ZrO_2$ - $Y_2O_3$  powders during isostatic compaction.

types of powder do consist, however, of relatively weak agglomerates which are completely collapsed after isostatic pressing at 400 MPa. If, during wet-chemical powder preparation, the free water is not removed thoroughly the agglomerates within the calcined powder do not collapse during compaction [5, 6] and those compacts do not densify easily during sintering. After compaction at 400 MPa the pores within the compact have a size distribution shown in Fig. 3. It can be seen from this figure that the pore radii within the alkoxide and chloride compacts are respectively smaller than 9 nm and 6 nm. The pores within the chloride compact have a mean radius of about 3 nm.

The alkoxide compact clearly shows a bimodal pore structure. In addition to the major size distribution at 4.5 nm radius a small shoulder in the pore radius region around 2 nm is detected (Fig. 3). The appearance of this bimodal pore size dis-

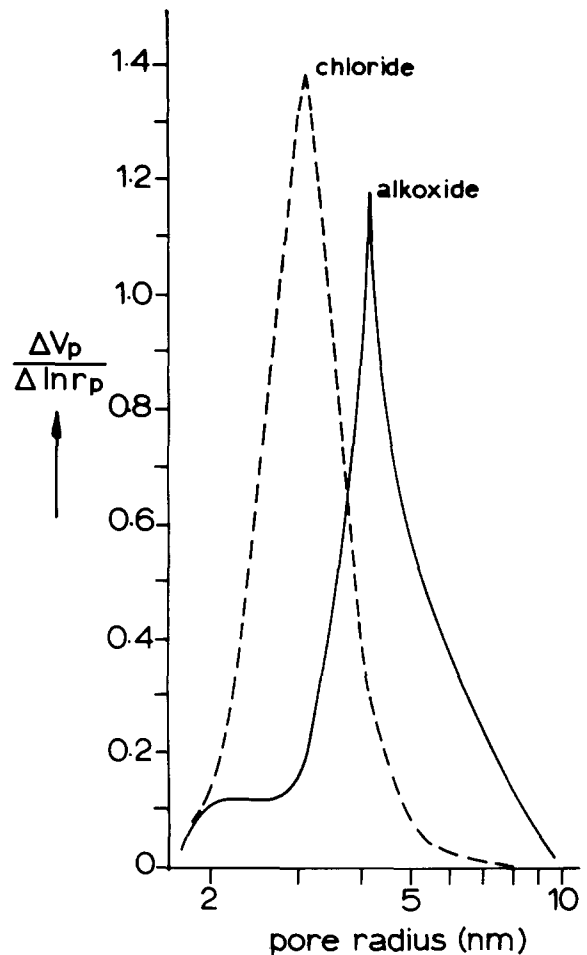


Fig. 3. Pore size distribution within the powder compacts after isostatic pressing at 400 MPa.

tribution could result from the presence of relatively small aggregates. These aggregates are built up from a small number of closely packed primary crystallites [6] and have a size of 15–20 nm and a relative density of about 70%. The pore radius within those aggregates is 2 nm. The two pore size ranges detected in the alkoxide compact originate from a packing of aggregates with *inter-aggregate* pores at 4.5 nm and a small shoulder 2 (nm) originating from the *intra-aggregate* pores. The presence of the dense aggregates within the alkoxide powders also explains the difference between crystallite size and equivalent BET crystallite diameter. The argon gas used for BET measurements cannot form a complete monolayer around the closely packed crystallites.

In the chloride compact no bimodal pore size distribution is observed after compaction at 400 MPa (Fig. 3). The crystallite size determined by X-ray line broadening fits well with the equivalent BET crystallite diameter. It can be concluded from both data that no aggregates are present in the chloride-derived powders.

The alkoxide and chloride compacts of tetragonal zirconia densify to 97% relative density after 10 h sintering at 1200 °C and 1050 °C respectively. The existence of the small aggregates within the alkoxide compact strongly influences the microstructural development during the first stages of sintering [4]. The difference in sintering behaviour between chloride and alkoxide compacts can possibly be ascribed to the absence or presence of aggregates. This may result in a difference in grain growth and pore morphology change during sintering of the compacts. This is discussed in detail in ref. 12.

The difference in powder morphology observed between the alkoxide and chloride powders is possibly caused by the wet-chemical powder preparative method. These methods are mainly distinguished by the different precursors used, an organic alkoxide solution vs. an inorganic chloride solution. The precursor and hydrolysing agent (water and concentrated ammonia for the alkoxide and chloride methods respectively) seem to have a great influence on the aggregate and agglomerate structure in the gel phase and in the final oxide powder.

#### 4. Conclusions

Ultra-fine-grained  $Y_2O_3$ -doped  $ZrO_2$  ceramic powders have been prepared by two different

hydrous gel precipitation techniques, the hydrolysis of metal alkoxides and metal chlorides. The powder properties (crystallite size, BET surface area, agglomerate strength and agglomerate density) are independent of both the amount of yttrium added and the crystal structure.

Several of these powder properties are dependent on the wet-chemical preparation method.

Both powders have a crystallite size of 8 nm.

The ceramic powders prepared by the hydrolysis of metal alkoxides consist of relatively weak and porous agglomerates. These agglomerates are built up from dense and relatively strong aggregates. This powder morphology can explain the bimodal pore size distribution within an alkoxide compact after isostatic compaction at 400 MPa.

The ceramic powders prepared by the hydrolysis of a metal chloride solution consist of stronger and more dense (relative density 30%) agglomerates. In these powders, however, no aggregate structure is observed. This is confirmed by the presence of one type of pore after compaction at 400 MPa and the similarity between the crystallite size and the equivalent BET crystallite diameter.

The agglomerates of both types of powder are weak enough to collapse completely during compaction prior to sintering.

The pore structure of the chloride compact is probably a better start for densification during sintering.

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