

# ZrO<sub>2</sub> Submicropowder Compaction Using Slip and Dry Methods

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#### Abstract

Three compaction methods of  $ZrO_2$  submicropowder: traditional uniaxial pressing, the pressure filtration method, and centrifugal compaction of slips using the HCP method (High-Speed Centrifugal Compaction Process), were compared. Pore size distribution of  $ZrO_2$  green compacts was measured using the method of mercury porosimetry. The most important influence on the HCP deposition process was expected by the centrifugal sedimentation conditions (velocity, duration of the process, dispersing agent) and the rotor geometry. The deposition process was carried out using an ultra-centrifuge with a rotational speed of 20000 rpm through 15 min for dispersive liquids of various pH. The influence of powder compaction method on properties of pressureless sintered  $ZrO_2$  compacts was analyzed. Micro-structure observations were performed by SEM, and Vickers hardness measurements, dependent on a distance from the top surface to the bottom surface of samples, were taken. The HCP powder compacts which are prepared by the traditional uniaxial pressing of powders. The samples compacted using the HCP and the pressure filtration method are characterized by the layering of properties and variations in hardness distribution. But in the HCP compaction material, there is a nonporous area which is transparent.

Keywords: Powder formation method, ZrO<sub>2</sub>, Mechanical properties, Microstructure - final

#### ZAGĘSZCZANIE SUBMIKRONOWEGO PROSZKU ZrO₂ METODAMI WYKORZYSTUJĄCYMI MASY LEJNE I SUCHE

Porównano trzy metody zagęszczania submikronowego proszku ZrO<sub>2</sub>: tradycyjne prasowanie jedoosiowe, prasowanie filtracyjne i odśrodkowe zagęszczanie masy lejnej przy użyciu metody HCP (*high-speed centrifugal compaction process*). Rozkład wielkości porów surowych wyprasek ZrO<sub>2</sub> zmierzono metodą porozymetrii rtęciowej. Najważniejszego wpływu na proces osadzania HCP upatrywano w warunkach sedymentacji odśrodkowej (prędkość, czas trwania, czynnik dyspergujący) i geometrii wirnika. Proces osadzania przeprowadzono z wykorzystaniem wirówki pracującej przy szybkości obrotowej 20000 obr/min, przez 15 min, w przypadku mas lejnych o różnym pH. Analizie poddano wpływ metody zagęszczania proszku na właściwości spiekanych swobodnie wyprasek ZrO<sub>2</sub>. Przeprowadzono obserwacje mikrostruktury za pomocą SEM oraz pomiary twardości Vickersa na przekroju badanych próbek, w kierunki ich prasowania. Zagęszczanie proszku ZrO<sub>2</sub> metodą HCP mocno zależy od pH masy lejnej. Największe wartości gęstości i twardości uzyskano w przypadku wyprasek ZrO<sub>2</sub>, które przygotowano metodą tradycyjnego, jednoosiowego prasowania proszku. Próbki HCP i prasowane filtracyjnie charakteryzowały się zróżnicowaniem właściwości zależnie od warstwy i zmianami w rozkładzie twardości. Jednakże, w materiale zagęszczanym metodą HCP występują nieporowate, transparentne obszary.

Słowa kluczowe: metoda formowania proszku, ZrO,, właśćiwości mechaniczne, mikrostruktura finalna

# 1. Introduction

The main aim of the presented study is to replace traditional uniaxial pressing or isostatic pressing with centrifugal compaction of slips of fine powders using the HCP method (High-Speed Centrifugal Compaction Process) or pressure filtration, especially for nanometric and submicrometric powders. For compaction of ceramic powders, dry processes, such as dry pressing and cold isostatic pressing, are very often used. Friction forces and stresses in the green bodies accompany dry pressing methods. The reliability of drypressed ceramics is limited by defects due to agglomerates [1]. Deformation and fracture of material particles is possible under compacting pressure [2]. In recent years, new techniques have been developed: hot isostatic pressing, aqueous injection moulding, direct coagulation casting, electrophoretic forming, gel-casting, hydrolysis assisted solidification, pressure filtration, temperature induced forming and others. These methods have benefits, but also disadvantages and limitations. Only a few of these methods are commercialized.

Wet (or colloidal) processing, such as slip casting, tape casting, pressure slip casting or pressure filtration, reduces friction between particles and prevents bridging of particles during compaction [2]. The high-speed centrifugal compaction process uses compacted powder from the slip. Material particles sediment under centrifugal force. The duration of compaction is short, due to a high compaction velocity. The HCP method involves low contamination during process [4].

In Suzuki's *at al.* work,  $Al_2O_3$  (mean particle size of 0.22 µm with narrow size distribution) green compacts made at low rotational speed were characterized by a low density and a density gradient [3]. The density gradient of most of the compacts can be eliminated by sufficiently high centrifugal force. Two process steps: drying and especially pre-sintering have an effect on the results of this study, but for the dried samples there was not a suitable method for the measurement of dried compact density. For the compacts formed at a speed of 11500 rpm, relative density was 63 %. A single heavy spherical particle falls in a viscous fluid under a gravitational field according to the Stokes settling velocity [4]:

$$U_{\rm s} = \frac{d^2(\rho - \rho_{\rm c})}{18\eta} g_0 \,, \tag{1}$$

where *d* denotes the diameter of the particle,  $\rho$  and  $\rho_c$  the densities of the particles and of the fluid,  $\eta$  the dynamic viscosity of the fluid, and  $g_o$  the gravitational acceleration. Formula (1) is valid for laminar flow, when the Reynolds number  $Re = \frac{U_s \rho d}{\eta}$  satisfies the inequality  $10^{-4} < \text{Re} < 2$  [4].

For slowly sedimenting particles, long-ranged hydrodynamic interactions lead to a correction to the Stokes settling velocity.

This is also the case for pressure filtration of slips. In both methods, particles are dispersed in water or other liquid to form a slip. Friction between particles is reduced and dense and homogenous packing is realized.

#### 2. Experimental procedure

Rotational speed was determined for submicrometer powders in the previous works [5]. For this work, submicrometer ZrO<sub>2</sub> powders produced by Tosoh Corporation (TZ-3Y, stabilized with 3 mol.% Y<sub>2</sub>O<sub>3</sub>, a specific surface of 16 m<sup>2</sup>/g) were used. Studies were carried out for rotational speeds from 15 000 to 25 000 rpm. The best consolidation of samples was obtained for the powders deposited at 20 000 rpm, using an ultra-centrifuge UP67 M, Germany. A Zetasizer Nano ZS by Malvern Instruments was used to measure zeta potential using the LDE method (Laser Doppler Electrophoresis). Pore size and pore size distribution of green compacts were measured using the method of mercury porosimetry and a PoreMaster 60, Quantachrome Instruments, USA. Hardness of the polished samples was determined by the Vickers method using a digital Vickers hardness tester (Future-Tech FM-7, Japan) with an indentation load of 4.95 N.

The most important influence on the HCP deposition process appeared in the centrifugal sedimentation conditions (velocity, duration of the process, dispersing agent) and the rotor geometry. The deposition process was carried out using the ultra-centrifuge with a rotational speed of 20 000 rpm through 15 min for dispersive liquids of various pH, which was changed by NaOH, CaCO<sub>3</sub> or CH<sub>3</sub>COOH addition. A geometrical scheme of the rotor is presented in Fig. 1. The rotor is an aluminium tubular vessel with a circular base. The distance between the centre of rotation and the top of the vessel is denoted by  $r_{min}$  and fixed equal to 5.5 cm. The distance to the bottom,  $r_{max}$ , is equal to 12.88 cm. Thus

the height of the vessel is 7.38 cm. The axis of rotation is perpendicular to the axis of the tube.



Fig. 1. Geometrical scheme of the rotor.

Besides the HPC method, powders were compacted using the pressure filtration method under 5 MPa and for a duration time of 6 hours. The sample diameter and height was 22 mm and 6 mm, respectively, for the filtration method.

Traditional uniaxial pressing in metal dies was the third method of compaction. The  $ZrO_2$  powders were dried and granulated. Bars of 16 mm in length and of thickness 5x5 mm were formed by single-action pressing under a pressure of 30 MPa and by isostatic pressing under a pressure 200 MPa.

After the forming processes, samples were dried at 498 K for 48 hours. Sintering was carried out at a heating rate of 2 K/min. Samples were held at 1770 K for 2 h.

#### 3. Results and discussion

The pH of the dispersing agent is one of the most important factors affecting the zeta potential of the aqueous media. The plot of zeta potential versus pH for  $ZrO_2$  colloidal suspensions is shown in Fig. 2.

The isoelectric point for these colloidal suspensions is approximately at pH 8.8; positive charge is sufficient for pH values less than 5.5 and longer than 10, when a negative charge is present. There are problems with coagulation and aggregate forming, when the zeta potential values are between +35 mV and -20 mV. The influence of aqueous media pH on pore size and pore distribution in green  $ZrO_2$  bodies is presented in Fig. 3. The results of  $ZrO_2$  centrifugal compac-



Fig. 2. Zeta potential versus pH for ZrO<sub>2</sub> particles in aqueous media.



Fig. 3. Pore size distribution for  $ZrO_2$  green bodies obtained using aqueous suspensions: sample 1 - pH 2.00; sample 5 - pH 4.70; sample 13 - pH 9.15 and samples axially pressed at pressures of 50 and 200 MPa.

Table 1. Density, pore size and distribution characterization for  $ZrO_2$  samples, compacted using the HCP method, are dependent on the pH of the aqueous media.

Sample number	[pH] of sample	Cumulative pore volume [mm³/g]	Percent of porosity [%]	median pore size distribution [nm]	mode pore size distribution [nm]	Delta* [nm]
1	2.00	196.2	55.79	57.19	56.38	0.81
2	3.00	211.5	55.09	58.76	59.23	0.47
3	3.50	206.2	55.62	64.20	58.28	5.92
4	4.20	163.1	49.92	41.68	35.79	5.89
5	4.70	153.1	47.31	37.08	34.40	2.68
6	5.25	155.4	49.64	37.84	34.22	3.62
7	5.75	157.5	50.81	40.97	33.31	7.66
8	6.10	196.3	51.65	46.74	39.60	7.14
9	7.10	178.2	51.26	45.78	36.67	9.11
10	7.60	191.5	52.97	47.81	37.25	10.56
11	8.10	193.3	51.78	46.26	41.14	5.12
12	8.58	186.4	53.33	47.55	42.34	5.21
13	9.15	167.7	51.28	54.18	50.40	4.22
P50	50 MPa	181.4	50.99	46.58	43.90	2.68
P200	200 MPa	140.4	42.38	37.63	36.62	1.01

\*) Delta - difference between mode and median values of pore size distribution - shows width of pore size distribution

tion are compared to those of axially pressed samples at pressures of 50 and 200 MPa and presented in Table 1. The best result was achieved for pH of 4.7. For axially pressed samples at 200 MPa, the pore size is approx. 37 nm. The results for the  $ZrO_2$  green bodies, obtained using aqueous suspensions of pH 2.0, 4.7 and 9.15, and the samples axially pressed at the pressures of 50 and 200 MPa are presented in Fig. 3. The best porosity distribution appeared in sample number 5 for aqueous suspension of pH 4.7. Pore distribution is monomodal; mode pore size is 34.4 nm for sample

5. Densities of the  $ZrO_2$  compacts both obtained using the HCP method and axially pressed at the pressure of 200 MPa are presented in Fig. 4.

Hardness HV 0.5 distributions for the three methods of compaction are presented in Figs. 5, 6 and 7.

The maximal values of hardness HV 0.5, for all  $ZrO_2$  samples, are around 1500.  $ZrO_2$  compact obtained using the HCP method is characterized by a hardness value decreasing towards the surface layer (Fig. 5). The reason for this phenomenon is the sample coming out adhesion between



Fig. 4. Densities of  $ZrO_2$  compacts using HCP method, dependent on duration of compaction and of  $ZrO_2$  compact using the uniaxial pressing method.



Fig. 5. Hardness distribution in the  $ZrO_2$  compact using the HCP method, dependent on height of sample (from top to bottom of the sample). Two measurements were made for each sample.



Fig. 6. Hardness distribution in the  $ZrO_2$  compact using the pressure filtration method, dependent on height of sample (from top to bottom of the sample). Two measurements were made for each sample.



Fig. 7. Hardness distribution in the  $ZrO_2$  compact using the uniaxial pressing method, dependent on height of sample (from top to bottom of the sample). Hardness distribution in the pressing direction.



20kU X5,000 5Mm 10 46 SEI b)

Fig. 8. SEM microstructure of  $ZrO_2$ ; a) the bottom area; b) the top area of sample.

bottom surface of tube and samples material, which has influence on no homogeneous porosity of compact.

Microstructures of the top and the bottom areas of the  $ZrO_2$  compact using the HCP method are presented in Figs. 8a and 8b. Except this surface porous layer (Fig. 8a), the material is characterized by a very homogenous hardness distribution and high hardness, and is transparent in the nonporous area.

The sample compacted using the pressure filtration method is characterized by the layering of properties and variations in hardness distribution. The minimal hardness value HV 0.5 for this sample is below 1300.

The most homogenous hardness distribution is for the uniaxially pressed sample.

# 4. Conclusions

Porosity and pore distribution of green bodies prepared by the HCP method are strongly dependent on pH of colloidal aqueous suspensions. The best results of pore size and distribution are obtained for the pH of 4.7.

The results of  $ZrO_2$  green body centrifugal compaction are comparable to those of axially pressed samples at the pressure of 200 MPa.

Densities and hardness distribution in  $ZrO_2$  compacts depend on the method of compaction. For  $ZrO_2$  compacts, the best properties were obtained for the uniaxial pressing method.

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