PII: S0955-2219(97)00197-0

Homogeneous Functional Ceramic Components through Electrophoretic Deposition from Stable Colloidal Suspensions—I. Basic Concepts and Application to Zirconia

Friedrich Harbach* and Hans Nienburg

ABB Corporate Research, PO Box 10 13 32, 69003 Heidelberg, Germany

Abstract

Usage of stable suspensions of deagglomerated fine powders is shown to be a prerequisite to take full advantage of the potential of electrophoretic deposition. The method is improved further when starting from suspensions which are additionally sieved through a 20 μm sieve into a 'cleansed and closed' deposition apparatus. Smooth zirconia tubes with green dimensions of 110 mm length, 0·5–1·5 mm wall thickness, 34 mm outer diameter have been produced under these conditions. The fired tubes had a characteristic strength of $\sigma_c = 420\,MPa$ and Weibull modulus $m = 15$, as calculated from burst pressure of whole tubes. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

A number of novel energy and environmental engineering systems are based on specific physical or physico-chemical properties of functional ceramic components. Among such systems are the amperometric oxygen-sensing lambda probe, the solid oxide fuel cell (SOFC), the sodium-sulfur high-energy battery and the alkali metal thermo-electric converter (AMTEC),[1] which all contain ion-conducting ceramics as the key functional components. These ceramics are sodium ion-conducting beta-aluminas in the latter two systems and oxygen ion-conducting zirconia in the former two.

These ceramic components must meet special functional requirements and reliability standards. The current-bearing capability is a central requirement to all of the functional ceramic components

under discussion. Other requirements, which are more or less common to them, are:[2]

- gas-impermeability, high relative density and phase purity;
- homogeneous high ionic conductivity, homogeneous current distribution (with no or negligible electronic conductivity);
- homogeneous thermal conductance, resistance to thermal cycling;
- high surface smoothness and resistance to corrosive or erosive attack;
- high dimensional accuracy, preferably at low wall thicknesses;
- high and reliable component strength, especially strength in the bonding area (where the ceramic component is joined to the metallic system);
- and, last but not least, ease of production with high reliability from small to large production rates.

Most of these requirements depend on homogeneity and flawlessness of the ceramic microstructure. They are better fulfilled the finer the microstructure is, i.e. smaller grain sizes and narrower grain-size distributions are desired. This leads to the following 'ceramic consequences':

- For the functional ceramics in question, homogeneity comes before strength.
- Strength, however, can be used as a straightforward, convenient basic test approach to check deviations from homogeneity and reliability targets.

For functional ceramics, especially for current-bearing functional ceramics, any desired strength increase should not be achieved through particle or

*To whom correspondence should be addressed.

fibre reinforcement (as it is being attempted for some advanced structural ceramics) or through incorporation of surface compressive stress (as often done with more classical ceramics). Any improvement of performance, including strength, should be achieved through increased homogeneity of microstructure and through reduction of flaw size.[3-6] To arrive at this goal, powder processing and consolidation methods have to be improved.

Gradual improvement of conventional powder processing and shaping methods, be it dry pressing or slip casting, will not be sufficient. Conventional powder processing and shaping methods all suffer from a principal draw-back: they rely on the usage of powders that are agglomerated more or less intentionally. The size of these agglomerates defines the order of magnitude of the size of stacking defects during consolidation. All other quality assurance methods (phase control, impurity content, control of the shaping process and of subsequent process steps) cannot surpass this limit or even heal any flaws.[3] A more substantial advancement in ceramic processing is required for the improvement of functional ceramic components with respect to performance, reliability and manufacturing costs.[1,7]

2 Basic Experimental Concepts

2.1 Powders and powder processing
The route to follow, which allows surpassing the principally negative effect of agglomerated powders on flaw creation and flaw size in ceramic components is the *'direct route'*[8,9] *of consolidation from well dispersed deagglomerated submicron powders suspended in a suitable liquid and stabilized by appropriate additives.* An essential advantage of this *wet processing of well deagglomerated fine powders* is the possibility to separate coarse particles above a predefined size limit or to select a desired range of particle size distribution prior to shaping and to do this with low size limits practically unattainable with dry powders.[8,10,11] Selection of powders and appropriate processing that allow for preparation of well dispersed deagglomerated submicron powder suspensions are a prerequisite for a successful 'direct route'. Selection of a powder with submicron size of primary particles alone is not sufficient.[12,13]

2.2 'Wet' forming

2.2.1 Sedimentation, pressure filtration or filter pressing
A principally successful approach to consolidation from a fine stable suspension is sedimentation.[12,14] However, this requires unacceptably long deposition times for fine particles which makes sense only

for scientific investigations and testing, but not for industrial applications.[9,14] Pressure filtration or filter pressing using membranes with micron- or submicron-sized filter pores as an advanced replacement for slip casting could be another way,[8-14] but would mean using costly filter bodies and high pressures, and thus limiting the manufacturability.

2.2.2 Electrophoretic deposition (EPD)
EPD is an electrokinetic process that has been known for quite some time.[14-23] It is the movement of charged particles and counterions—suspended in a liquid—under the influence of an electric field. Under applied electric fields, these particles may travel between two electrodes and deposit at one of them. Fundamentals of the EPD process need not be discussed here, as they have been presented several times elsewhere.[16,18,20,24]

The EPD process has an important advantage against other colloidal consolidation methods. The deposition rate is nearly independent of particle size and of thickness of the deposited layer. As opposed to filtration processes, no movement of the solvent through the deposited layer is required (excepting possible electroosmotic side-effects within the deposited layer). Thus high deposition rates can be achieved for very fine particles and thick layers.

The essential prerequisite for successful electrophoretic deposition is the electrical charging of the suspended solid particles. Such charging may occur through selective dissolving of ions and/or through adsorption (physi- or chemisorption) of ionic compounds onto the surface of the solid particle, creating an electric double layer at the surface of the solid particle. The electric double layer serves a double function: to stabilize the suspended particles (electrostatic stabilization) and to allow movement of the particles in an electric field.

Electrostatic stabilization is easiest in water, but electrophoretic deposition in aqueous suspensions is subject to the electrolysis of water at potentials above 2 V. Without additional measures such as reactive electrodes[17] or intermediate membranes,[25] the resulting gas bubbles would be incorporated into the consolidated green body, thus reducing its microstructural homogeneity. Such problems can be avoided by using organic solvents as suspension media for EPD.

Plates and tubes were selected for the forming experiments.[8,9,11] The preparation of plates is much simpler and on the whole much faster than the fabrication of tubes. Thus, the fabrication of plates became the preferred method for the testing of suspension behaviour and other initial or preparative testing and selection steps. Investigations of the shaping process and strength testing have been done with tubes, as tubes are presently

the preferred choice for the above-mentioned energy and environmental engineering systems.

2.3 Quality assurance

The achieved level of improvement of ceramic quality cannot be quantified significantly by average values (average grain size, average pore size, average surface roughness etc.). Rather, quality control must focus on the reduction of extreme values of flaw sizes. The level of reduction should be checked preferentially over the whole volume or surface of the manufactured body.

Large inhomogeneities within the bulk of a ceramic body can be detected reliably only by means of tensile strength testing. Internal burst testing of tubes is a sufficient alternative to tensile stress conditions and has the advantage of being a relatively quick and simple test method. To detect fracture origins, each strength test was followed by fractographic analysis.

2.4 Scope of this paper

EPD of ceramic components is known to be applicable on an industrial scale.[17,19,21,23,25] Convincing results regarding cost effectiveness and reliability are, however, still missing. Usage of aqueous suspensions[17,25] or of non-aqueous, but non-stabilized suspensions[21,23] or not sufficiently stabilized suspensions[19] are the major draw-backs of these known concepts.

First results of the application of EPD to stabilized non-aqueous suspensions of fine alumina powders have been published previously by the authors.[8,9,11] The authors report here a combination of submicron powders, polar protic solvents and ionic organic dispersants that show the best results for zirconia regarding long-term stability of suspension and electrophoretic mobility. It is this combination of EPD and stable suspensions from deagglomerated fine powders that distinguishes the approach of the authors from other EPD work.[19,21,23] To assure the positive effect of deagglomeration of suspensions and to further reduce flaw sizes, sieving and cleansing steps were later introduced into the production process.

In a second paper,[26] the same approach will be applied to beta-alumina functional ceramic components. In addition, the experimental procedure will be developed towards industrial-scale manufacturing and estimates of costs are given.

3 Experimental Methods

3.1 Powders and powder processing

Hüls DZF-8Y was used as pre-reacted zirconia partially stabilized with 5 mol% Y_2O_3. A few early

investigations of particle size distributions were done also using Lonza 8Y-FSZ and Tosoh TZ-8Y fully stabilized zirconia powders with 8 mol% Y_2O_3. Characteristics of the selected powders are summarized in Table 1.

Generally, dispersing systems were chosen with as few organic constituents of low volatility as possible, as to limit problems in the later firing stage. For this paper, only organic solvents were investigated. Alcohols, mostly ethanol and 2-propanol, were used for these investigations. Different oligomeric or polymeric ionic or polar organic compounds were tested as dispersing and charging aids (Table 2). Dispersing aids with an inherent binding effect (copolymers) were preferred so that the addition of special binders for increased green strength of the consolidated bodies could be avoided.

The dispersion of above powders was supported through ultrasonic agitation (Branson Sonifier BI 30, 200 W). Sedimentation or centrifugation was used for separation of larger particles or agglomerates.

3.2 Electrophoretic deposition

3.2.1 Basic conditions

Electrophoretic deposition of plates[9] and tubes was done in separate apparatuses (Fig. 1). For the fabrication of tubes, an internal deposition approach was used.[27] Typical deposition conditions were: voltage of 140 V, electric field strength of 100 V/cm, current of 2 mA, current density of $20 \mu A cm^{-2}$. Under these conditions, a deposition rate of $1.3 mm min^{-1}$ resulted for suspensions with 60 mass% (16.7 vol%) zirconia (Hüls DZF-8Y) in 2-propanol and with acrylate-acrylamide copolymers as dispersants. The deposition electrodes used for all investigations reported in this paper were made from stainless steel with polished surfaces.

3.2.2 'Cleansed and closed' apparatus

The suspensions were sieved into the closed deposition chamber using $20 \mu m$ stainless steel sieves to help ensure that no dust could enter the chamber and to keep out any residual agglomerates and coarser powder particles. In addition, the deposition apparatus and tubing were cleansed thoroughly prior to sieving in the suspension, applying the same organics for cleansing as were used as dispersing media.

3.3 Drying and sintering

After forming, the residual suspension was poured off. Then the green bodies were dried. Drying of electrophoretically deposited components was especially quick and straight-forward when acrylic

Table 1. Characteristics of the zirconia powders selected for this investigation

Y_2O_3 content	Producer	Particle size distribution			BET surface area	Purity
		Nominal[a]		Measured[b]		
Mass%		d_{50} (μm)	Primary particle size (μm)	d_{50} (μm)	(Supplier data) ($m^2 g^{-1}$)	(Supplier data) (%)
9.3 (including 1·8 mass% HfO$_2$)	Hüls DZF-8Y	0·6		0·9	8·5	99·9
14·3	Lonza 8Y-FSZ			0·7	10	99·9
13·4	Tosoh TZ-8Y	0·3	0·025	1·56	16	99·9

[a]Supplier data.
[b]Measured in suspension (see Section 3.4).

Table 2. Stability and suitability for electrophoretic deposition of ZrO$_2$ (DZF-8Y) suspensions (data from sedimentation tests with 10 vol% powder and 1 mass% dispersion aid; after sedimentation time of 21 days)

Dispersion aid (producer)	Solvent/suspension behaviour top: visual appearance; centre: stability characterization (+ stable; ± medium; —instable) and suitability for electrophoretic deposition [E good: (E): possible]; bottom: sediment density	
	Ethanol	2-Propanol
Without	Clear	Clear
	—	—
	1·5 g cm^{-3}	1·5 g cm^{-3}
4-Hydroxybenzoic acid (Merck-Schuchardt)	Very turbid	Very turbid
	+, E	+, E
	3·3 g cm^{-3}	3·3 g cm^{-3}
Poly-acrylic acid salt (Zschimmer + Schwarz, Dolapix PC33)	Very turbid	Clear
	+	—
	3·0 g cm^{-3}	1·0 g cm^{-3}
(Acrylic acid-acrylate) copolymer (Röhm, LP 10466/12B)	Very turbid	Turbid
	+, (E)	±, (E)
	2·7 g cm^{-3}	1·5 g cm^{-3}
(Acrylate-acrylamide) copolymer (Röhm, LP 10466/9B)		Very turbid
		+, E
		2·7 g cm^{-3}
Poly-ethylenimine (Aldrich)	Very turbid	Very turbid
	+	+, (E)
	3·3 g cm^{-3}	3·0 g cm^{-3}

copolymers were used, due to their supportive binding action: 30 min pre-drying at ambient temperature, then removal of the compacts from the electrodes, plus 15 min drying at 50 to 70°C. Firing at ambient atmosphere in electrically heated furnaces (Naber HT 16/17, Naber Industrieofenbau, Lilienthal/Bremen, Germany) was applied, with maximum temperatures for densification ranging from 1450 to 1500°C (heating rate 5 K min^{-1}, holding time 4 h).

3.4 Quality assurance and characterization methods

Sedimentation behaviour of powder suspensions were investigated using 10 vol% of powder and 1 mass% of dispersing aid (relative to the powder) and 50 to 100 ml scaled laboratory cylinders. Viscosity and flow behaviour were checked with rotating viscometers (Haake Rotavisco RV 20,

Haake-Fisons, Karlsruhe, Germany) and a coaxial cylinder measuring device (Mooney-Ewart, Haake-Fisons, Karlsruhe, Germany).

A laser light diffraction apparatus (Cilas Granulometer HR 850-B, Cilas, Marcoussis, France) was used to measure particle size distributions of powders in suspensions. As typical for this method, diluted suspensions were used for these measurements. The solvent for dilution had the same dispersant concentration as the starting powder suspension.

Electrophoretic mobility was checked via the moving boundary method in preparatory experiments (custom-made apparatus). In the final stages of this investigation, electrophoretic performance of powder suspensions was just checked by evaluating the deposition of plates.

Pore size distributions of green bodies were measured through mercury pressure porosimetry[28]
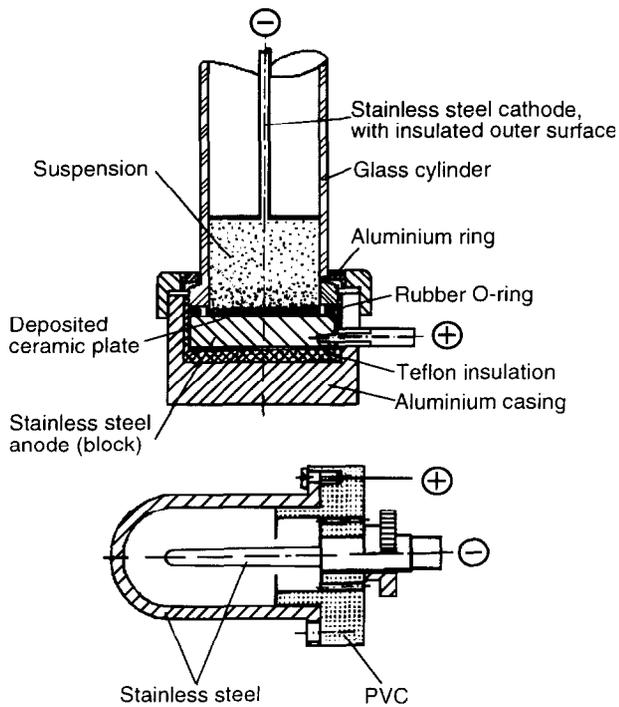
Fig. 1. Schematic drawing of apparatus for electrophoretic deposition of plates (above) and for internal electrophoretic deposition of closed-end tubes (below).

(High Pressure Porosimetry, Carlo-Erba Instruments, Milan, Italy). Green densities were measured with mercury pycnometry (using the macropore unit 120 of the afore-mentioned instrument), fired density with mercury pycnometry or buoyancy measurement in water.

Strength testing was done using internal burst pressurization of whole tubes. Hydraulic pressure was used to press a silicone tube against the inner surface of the ceramic tube. To facilitate later fracture analysis, the outside surface was covered with thin adhesive tape.

Fractographic analysis was performed by a visual crack analysis to detect the location of the fracture origin, followed by inspection using optical and scanning electron microscopy techniques to identify the nature of the fracture origin. As long as the size of the fracture-originating flaw is still substantially larger than grain size, micrographs are of little relevance for the scope of this paper. They are, therefore, not used in this paper. Grain size of fired bodies will be given only to indicate grain growth from sintering.

4 Results and Discussion

4.1 Powders and powder processing

4.1.1 Suspension behaviour

A simple sedimentation test[9] is the easiest approach to check the principal applicability of powders, suspension media and dispersing agents. In the case of zirconia suspensions, unstabilized, agglomerated powder suspensions coaggulate within a few hours to a voluminous sediment. The phase boundary between the sediment and the clear superseding solvent phase moves downwards gradually, but the sediment will not densify beyond a density of 0·9 to 1·5 g cm^{-3}. Well stabilized, deagglomerated suspensions remain turbid over weeks, and a relatively dense sediment (3·0 to 3·3 g cm^{-3}) is slowly built up from bottom to top. Intermediate supensions show mixed behaviour, i.e. a sediment which accumulates from bottom to top, but with a rather poor density of 2·1 to 2·7 g cm^{-3} due to residual agglomerates, and a superseding suspension, which may remain slightly turbid over 1 to 2 weeks.

Zirconia suspensions may be stabilized best using polar-protic solvents, such as ethanol or 2-propanol, together with dispersing aids with polar or ionic groups such as 4-hydroxybenzoic acid, (acrylic acid/acrylate) copolymer, (acrylate/acrylamide) copolymer or poly-ethylenimine (Table 2). It may be assumed that hydrogen bonds between solvent and particle surface play a dominating role. Polar-aprotic and unpolar solvents, such as ketones or toluene or other aromatic hydrocarbons are not effective.

Regarding electrophoretic mobility and deposition behaviour, screening experiments were performed with quite a few stable and intermediate
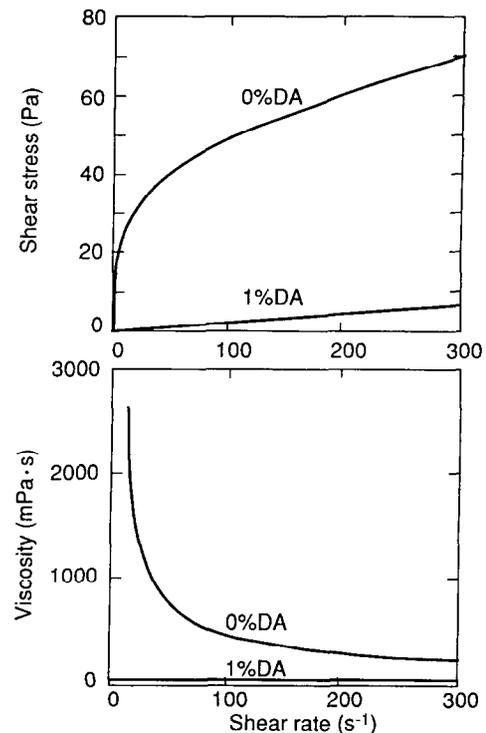

Fig. 2. Flow (above) and viscosity (below) curves for zirconia suspensions (70 mass% powder in ethanol), with and without dispersing aid (DA = 4-OH benzoic acid, concentration is given in mass% of DA per powder mass in a suspension).

F. Harbach, H. Nienburg

stable suspensions using the plate-type deposition apparatus.[9] In Table 2, the best performing suspensions of these are designed + E, i.e., stable as well as well suitable for electrophoretic deposition. Details of the composition of those suspensions investigated further (powder material and concentration, solvent, dispersing aid and concentration) will be given below in connection with specific discussions.

4.1.2 Viscosity

Viscosity measurements are another important method to characterize suspensions and to optimize dispersant concentrations and powder content. Typical flow and viscosity curves for zirconia supensions are shown in Fig. 2. Without addition of a dispersing agent, powder particles tend to agglomerate, enclosing dispersion medium and thus effectively reducing the amount of liquid which can be subjected to shear forces. The result is an increased viscosity compared to a well dispersed system. The agglomerated system shows the typical behaviour of a structural viscous liquid. Viscosity decreases with increasing shear rate, as more and more agglomerates are being destroyed through increasing shear stress. If, however, an appropriate dispersing agent is introduced, the suspension behaves nearly like a Newtonian liquid, i.e. its viscosity becomes independant of shear rate and shear stress increases linearly with shear rate (up to a solids content of around 70 mass%).
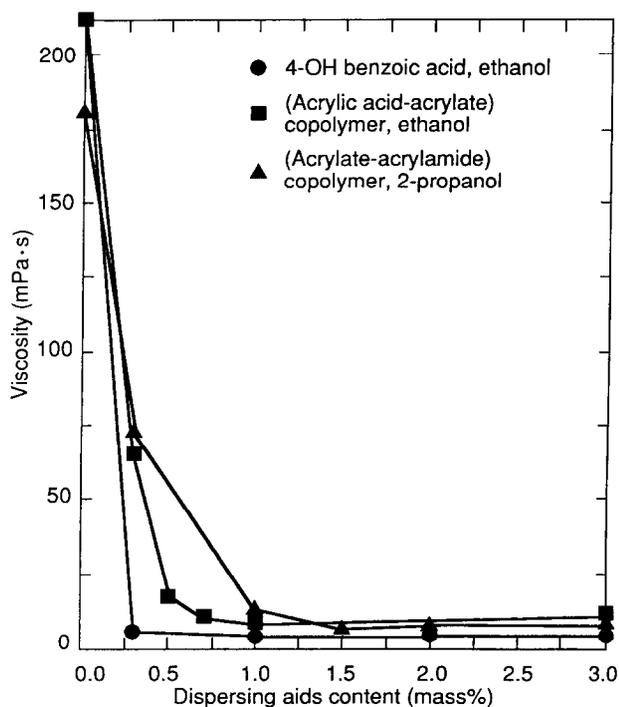

Fig. 3. Influence of three different dispersing agents on viscosity of a zirconia suspension (70 mass% of powder in ethanol or 2-propanol; addition of dispersing agents is given in mass% relative to powder mass in the suspension; shear rate $200 \, s^{-1}$).
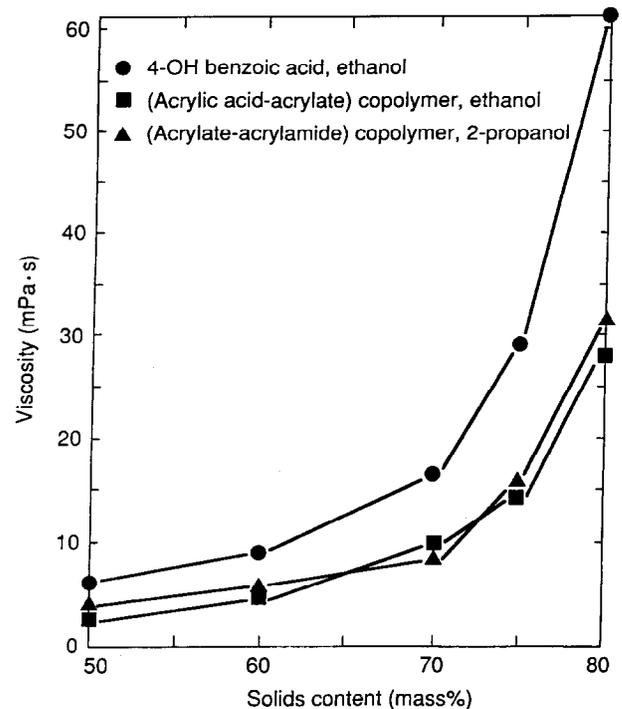

Fig. 4. Influence of solids content on viscosity of zirconia suspensions for three different dispersing aids [solvents: ethanol or 2-propanol; 1.5 mass% (relative to powder mass) of dispersing aid; shear rate $200 \, s^{-1}$].

For the stable and medium stable zirconia suspensions, as found from the above sedimentation tests, dependence of viscosity was measured at a shear rate of $200 \, s^{-1}$ for different contents of dispersion agent and for solids concentrations between 60 and 80 mass%.

Influence of different dispersing agents on viscosity of a zirconia suspension is given in Fig. 3. With appropriate dispersing agents (4-OH-benzoic acid, solvent ethanol), addition of such an agent can be kept as low as 0·2 mass% to assure a low viscosity. The viscosity remains low over an extended range of contents of dispersion agent. For polyelectrolyte–solvent combinations such as (acrylic acid/acrylate) copolymer in ethanol, slightly higher addition (above 0·5 mass%) is needed to assure a minimum of viscosity. The advantage of polymer dispersants, however, is the binding effect associated with them.

With suitable dispersants, the solids content may be increased to 80 mass% (40 vol%) with still acceptable thinly flowing and pourable suspensions (viscosity below 100 mPas at a shear rate of $200 \, s^{-1}$; see Fig. 4).

4.1.3 Particle size distribution and assessment of powders

The effect of different zirconia raw materials on particle size distribution of dispersed powder suspensions is shown in Fig. 5. The Hüls and Lonza powders with their comparable specific powder
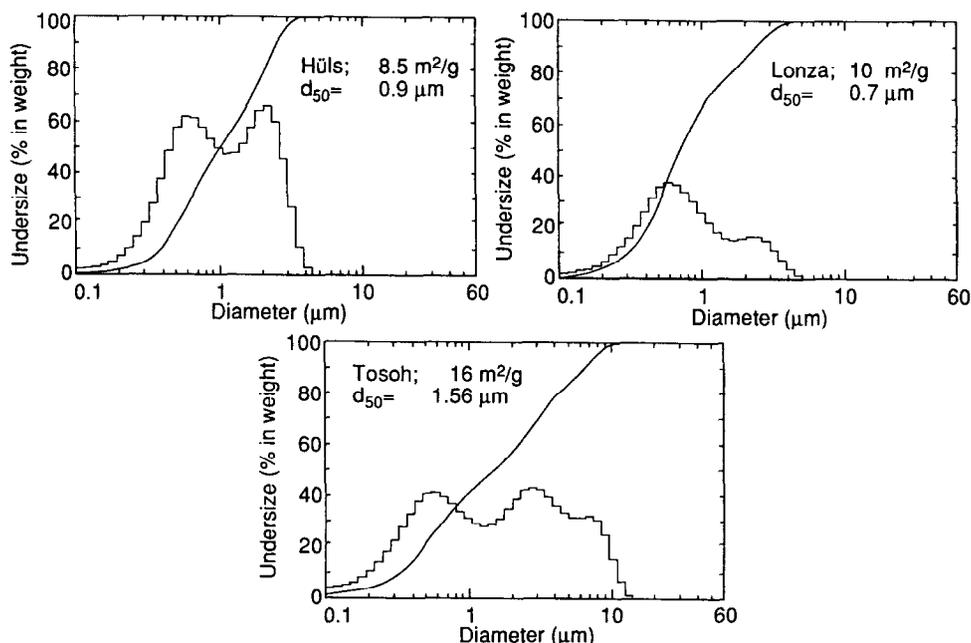
Fig. 5. Particle size distribution of three different zirconia raw materials in ethanol with 4-OH benzoic acid as dispersant.

surface area (cf., Table 1) also show comparable size distribution of the suspended powder particles. The mean particle size is between 0·7 and 1 μm for both powders, and the maximum particle size is below 5 μm. (The distinct bimodal appearance of the particle size distribution curves of both powders have not been considered in greater depth within this investigation.) The Tosoh powder with its higher powder surface area is found to have a mean particle size of 1·6 μm with maximum particle size above 10 μm. Obviously, this powder cannot be deagglomerated with the means applied in the course of this investigation or it tends to reagglomerate after dispersion due to its higher surface area. The reason for the different behaviour of the Tosoh powder was not investigated further within this study.

The most convincing results regarding electrophoretic mobility and green-body stability were achieved with Hüls zirconia powder suspended in 2-propanol with 1·5 mass% (relative to powder mass) of (acrylate–acrylamide) copolymer. This suspension was used as a standard for the preparation of zirconia components.

4.2 Characterization of deposited, dried and sintered bodies

Sizes of the deposited green bodies were 50 to 100 mm diameter and 1 to 5 mm thickness for plates and 110 mm length, 34 mm diameter and 0·5 to 1·5 mm wall thickness for tubes. Electrophoretically produced and sintered zirconia components (tubes and plates) are shown in Fig. 6. The outstanding surface quality of zirconia ceramic bodies produced via electrophoretic deposition

from stable suspensions (without any post-treatment) can be readily seen. The zirconia bodies are slightly colored due to iron impurities in the raw powder.

The green density of electrophoretically shaped bodies is 58·5% (3·51 g cm^{-3}), fired densities (4 h at 1500°C) are 5·97 g cm^{-3}, 99·5% of theoretical
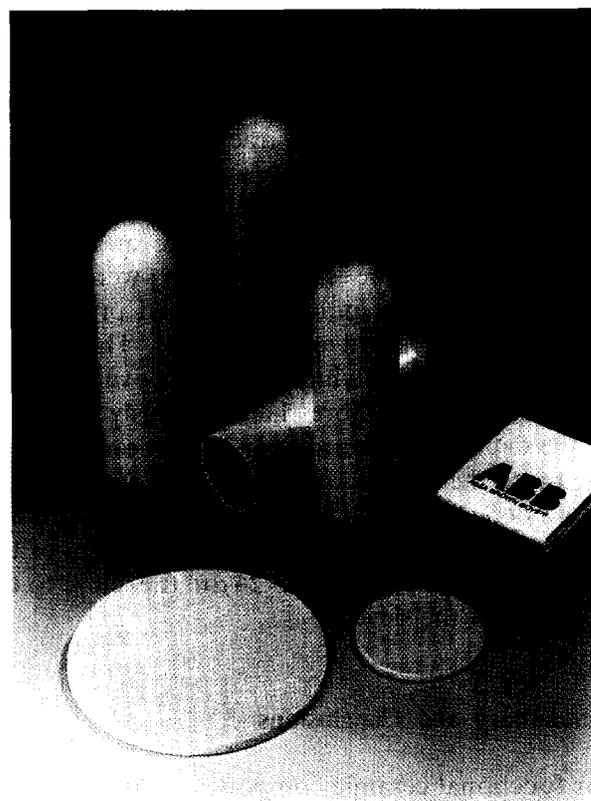

Fig. 6. Electrophoretically produced and sintered zirconia components (tubes and plates; match box dimensions $50 \times 5 \times 50$ mm^3 length/width/height).
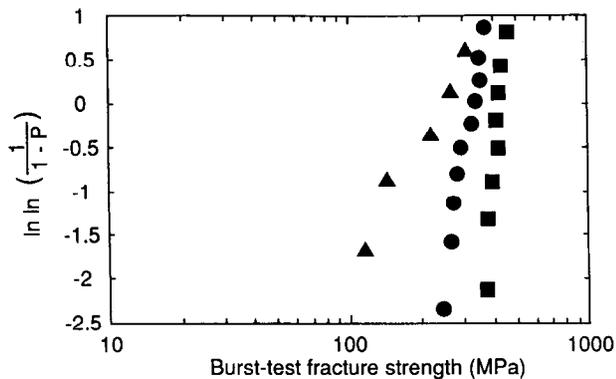
Fig. 7. Strength data (internal pressurization) for zirconia tubes originating from different electrophoretic manufacturing processes [▲: electrophoretically shaped from stable suspensions in open vessel, unsieved ($\sigma_c = 240$ MPa; $m = 3$); ●: electrophoretically shaped from sieved stable suspensions in closed vessel ($\sigma_c = 320$ MPa; $m = 9$); ■: electrophoretically shaped from sieved stable suspensions in 'cleansed and closed' vessel ($\sigma_c = 420$ MPa; $m = 15$); P = probability of fracture].

density. Average grain size of sintered material is in the range of 0·5 to 0·7 μm.

For strength testing purposes, three sets of electrophoretically deposited tube samples were produced, (a) from untreated suspensions, (b) from sieved suspensions (sieved through 20 μm sieves), (c) from suspensions that had been sieved through 20 μm sieves into the thoroughly cleansed closed deposition apparatus. Figure 7 clearly shows the positive effect of a 'cleaner' processing approach. The characteristic strength (from burst testing) increased from 240 MPa (with a Weibull modulus $m = 3$) over 320 MPa ($m = 9$) to 420 MPa ($m = 15$) for the three processing techniques.

The average size of the fracture origins for the 'sieved' tubes was 105 μm, which means it was still substantially larger than the mesh size of the sieve. Except for one case, all flaws were at the outer (electrode-side) tube surface. They were mostly lengthy, vermicular pores, which had presumably been caused by burnt organic fibres. These fibres are part of the dust which is present overall in the environment; some fibres had obviously remained on the deposition electrode and had been incorporated into the surface of the green body. Cleansing of the deposition apparatus prior to filling of the powder suspension reduced the average size of the fracture originating flaws to 24 μm (i.e. close to the mesh size of the sieve).

5 Summary and Conclusions

For functional ceramic components with increased requirements on microstructural homogeneity, wet shaping from fine stable powder suspensions is advantageous to overcome quality deficiencies

inherently connected with dry powder pressing or conventional slip casting. Use of submicrometer powders for preparation of stable fine powder suspensions is at the same time practically feasible and by far sufficient, making finer powder approaches (sol–gel or nanosized powders) unnecessary for the applications discussed.

Electrophoretic deposition (EPD) is a forming method which fits the above requirements. Best results have been achieved under controlled conditions comprising preparation of deagglomerated and fractionated stable powder suspensions and filtration into closed cleaned deposition vessels.

After previous investigations regarding consolidation of alpha alumina components, the method has now been applied to components made from zirconia powders. Starting from 'sieved' suspensions (through a 20 μm sieve) and with a cleansed deposition apparatus, smooth zirconia tubes (green dimensions of 110 mm length, 0·5–1·5 mm wall thickness, 34 mm outer diameter) with characteristic strength of $\sigma_c = 420$ MPa and Weibull modulus $m = 15$ (calculated from burst pressure of whole tubes) resulted under such conditions.

Investigations regarding fabrication of beta alumina ceramic components through EPD from fine stable suspensions are reported in a subsequent paper.[26]

References

1. Harbach, F., Schumann, B. and Rohr, F.-J., Funktionskeramik für die Energie- und Umwelttechnik. *Bull. SEV/VSE*, 1990, **81**(15), 9–14.
2. Harbach, F., Hochleistungs-Funktionskeramik für die rationelle, schadstoffarme und sichere Energieversorgung. In *2. Symposium Materialforschung 1991 des Bundesministers für Forschung und Technologie, Vorträge und Poster*, (*2nd Symposium Materials Research 1991 of the Federal*

Minister for Research and Technology, Presentations and Posters), ed. Projektträgerschaft Material- und Rohstofforschung (PLR). Forschungszentrum Jülich GmbH, Jülich, 1991, pp. 961-964.

3. Harbach, F. and Weiler, L., Microstructural inhomogeneities–causes and means of control. *cfi/Ber. DKG*, 1986, **63**(3), 107–113 (part 1), (6), 305–310 (part 2), (7/8), 406–409 (part 3).

4. Barringer, E., Jubb, N., Fegley, B., Pober, R. L. and Bowen, H. K., Processing monosized powders. In *Ultrastructure Processing of Ceramics, Glasses and Composites*, ed. L. L. Hench and D. R. Ulrich. John Wiley and Sons, New York, NY, 1984, pp. 315–333.

5. Aksay, I. A., Principles of Ceramic Shape-Forming with Powder Systems. In *Ceramic Powder Science IIB, Ceramic Transactions*, Vol. 1, ed. G. L. Messing, E. R. Fuller and H. Hausner. American Ceramic Society, Westerville, OH, 1988, pp. 663-674.

6. Yeh, T. S. and Sacks, M. D., Low-temperature sintering of aluminum oxide. *J. Am. Ceram. Soc.*, 1988, **71**(10), 841–844.

7. Bush, D. R., Designing ceramic components for structural applications. *Journal of Materials Engineering and Performance*, 1993, **2** (6), 851–862.

8. Harbach, F., Advanced production processes for high-tech ceramics, *ABB Review*, (4) 1990, 17–22 also *Materials & Design*, **11**(5), 1990, 257–261.

9. Harbach, F., Neeff, R., Nienburg, H. and Weiler, L., Reliable ceramic components from colloidal suspensions. *cfi/Ber. DKG*, 1990, **67**(4), 130–135.

10. Nienburg, H. and Harbach, F., Pressure filtration of fine ceramic suspensions. In *Ceramic Powder Science IV, Ceramic Transactions*, ed. S. Hirano, G. L. Messing and H. Hausner. American Ceramic Society, Westerville, OH, 1991, pp. 321–327.

11. Harbach, F., Neeff, R., Nienburg, H. and Weiler, L., Homogeneous ceramic components from colloidal suspensions. In *Ceramic Powder Processing Science, Proceedings of the Second International Conference*, ed. H. Hausner, G. L. Messing and S. Hirano. Deutsche Keramische Gesellschaft, Köln, 1989, pp. 609–616.

12. Nienburg, H., Stein, P. and Harbach, F., Wet shaping of fine-grained, homogeneous α-Al$_2$O$_3$ ceramics. *cfi/Ber. DKG*, 1989, **66**(5/6), 189–197.

13. Krell, A. and Blank, P., The influence of shaping method on the grain size dependence of strength in dense submicrometre alumina. *J. Eur. Ceram. Soc.*, 1996, **16**, 1189–1200.

14. Nienburg, H., Stein, P. and Harbach, F., Wet Chemical Forming and Characterization of Alpha-Alumina Ceramics. In *Ceramic Powder Science IIB, Ceramic Transactions*, Vol. 1, ed. G. L. Messing, E. R. Fuller and H. Hausner. American Ceramic Society, Westerville, OH, 1988, pp. 741–748.

15. Patai, E. and Tomaschek, Z., Die Herstellung und Untersuchung von Oxydkathoden von kolloider Struktur. *Kolloid-Z.*, 1936, **74**(3), 253–265.

16. Hamaker, H. C., Formation of a deposit by electrophoresis. *Trans. Faraday Soc.*, 1940, **36**, 279–287.

17. Händle, F., Elektrophoretische Verformung von keramischen Materialien. *Keramische Zeitschrift*, 1980, **32**(4), 185–188.

18. Hennicke, J. and Hennicke, W., Formgebung in der Keramik, II. Formgebung durch Abscheidung aus Schlickern im elektrischen Feld (Elektrophorese). In *Handbuch der Keramik* (Handbook of Ceramics). Verlag Schmid GmbH, Freiburg i. Br., 1981, pp. 13-23.

19. Mizuguchi, J., Sumi, K. and Muchi, T., A highly stable nonaqueous suspension for the electrophoretic deposition of powdered substances. *J. Electrochem. Soc.*, 1983, **130**(9), 1819.

20. Hiemenz, P. C., *Principles of Colloid and Surface Chemistry*. Marcel Dekker, Basel and New York, 1986.

21. Powers, R. W., Ceramic aspects of forming beta alumina by electrophoretic deposition. *Ceramic Bulletin*, 1986, **65**(9), 1270–1277.

22. Naß, R., Storch, W., Schmidt, H., Harbach, F., Neeff, R. and Nienburg, H., Electrophoretic deposition of alumina from non-aqueous dispersions. In *Ceramic Powder Processing Science, Proceedings of the Second International Conference*, ed. H. Hausner, G. L. Messing and S. Hirano. Deutsche Keramische Gesellschaft, Köln, 1989, pp. 625–632.

23. Heavens, S. N., Electrophoretic deposition as a processing route for ceramics. In *Advanced Ceramic Processing and Technology*, Vol. 1, ed. J. G. P. Binner. Noyers Publications, Park Ridge, New Jersey, 1990, pp. 255–283.

24. Sarkar, P. and Nicholson, P., Electrophoretic deposition (EPD): mechanisms, kinetics, and application to ceramics. *J. Am. Ceram. Soc.*, 1996, **79**(8), 1987–2002.

25. Clasen, R., Forming Compacts of Submicron Silica Particles by Electrophoretic Deposition. In *Ceramic Powder Processing Science, Proceedings of the Second International Conference*, ed. H. Hausner, G. L. Messing and S. Hirano. Deutsche Keramische Gesellschaft, Köln, 1989, pp. 633–640.

26. Harbach, F. and Nienburg, H., Homogeneous functional ceramic components through electrophoretic deposition from colloidal suspensions—II. Beta-alumina and concepts for industrial production. *J. Eur. Ceram. Soc.*, 1998, **18**, 685–692.

27. Neeff, R., Lindman, E. and Herschel, P., Verfahren zur Herstellung eines Formkörpers aus Oxidkeramik. EP 0324972, 1988.

28. Harbach, F. and Nienburg, H., Mercury pressure porosimetry as an accessory to the development of shaping and firing techniques for dense ceramic components. *cfi/Ber. DKG*, 1987, **64**(6/7), 226–230 (part 1), (10), 394–397 (part 2).

29. Drüsedau, K., Drumm, R., Knödler, R., Naß, R., Nienburg, H. and Riedel, H., *Homogene funktionskeramische Bauteile aus kolloiddispersen Systemen* (Homogeneous Functional Ceramic Components From Colloid-dispersed Systems). Bundesministerium für Forschung und Technologie (BMFT)—Materialforschung, Bonn, Germany, Final Report 03 M 2711 8, 1993.