PII: S0955-2219(97)00174-X

Homogeneous Functional Ceramic Components through Electrophoretic Deposition from Stable Colloidal Suspensions—II. Beta-Alumina and Concepts for Industrial Production

Friedrich Harbach* and Hans Nienburg

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

Abstract

Electrophoretic deposition of deagglomerated fine stable powder suspensions in a 'cleansed & closed' deposition apparatus has been shown to be a successful method to shape beta-alumina functional ceramic tubes. The novel method increased the strength and surface smoothness significantly compared to dry pressing. Introduction of appropriate dispersants helped to avoid drawbacks connected with those electrophoretic deposition methods hitherto tested for production of beta-alumina ceramics. A new multi-tube deposition apparatus was designed and tested. It could make electrophoretic deposition become competitive as an industrial-scale manufacturing method. © 1998 Elsevier Science Limited. All rights reserved

1 Introduction

General background of the investigations within this paper and the basic concept of *direct wet forming* through electrophoretic deposition (EPD) from *stable* colloidal suspensions under 'cleansed & closed' conditions, are described in a preceding paper dealing with deposition of zirconia functional ceramic components from stabilized fine zirconia powder suspensions.[1] The present paper demonstrates the application of this novel approach to beta-alumina powder suspensions and beta-alumina functional ceramic components. It concentrates on specifics of the powder processing and EPD process due to the alkaline nature of beta-alumina. Attention is given to the selection of appropriate dispersing systems. In addition, a bench-lab scale industrial-type electrophoretic manufacturing method is tested, which is based on the usage of stable powder suspensions.

EPD is not a new forming method (cf. the preceding paper[1] and references therein). Also, the application of EPD in the forming of beta-alumina ceramics is not a new method; it has already been followed towards industrial-scale manufacturing.[2–6] These latter developments, however, have suffered from use of agglomerated powders or otherwise non-stabilized suspensions. Their quality levels were not significantly better than those from conventional slip casting or dry-pressing approaches. The resulting ceramic components suffered from reduced reproducibility and reliability through unsatisfactory broad strength distributions. Extended proof-testing of each component or reduction of component sizes[6] are necessary to assure acceptable strength levels meaning higher cost in any case.

The present paper presents a comparison of the novel approach to the established dry pressing procedure with strength testing following the principle of testing of whole unmachined components of comparable size.[1]

2 Experimental Methods

Only those experimental means and methods will be presented in this section that have not been described previously[1] or where specifics regarding beta-alumina are to be reported.

2.1 Powders and powder processing

2.1.1 Powders
The beta-alumina powders used were standard reacted sodium magnesium polyaluminate

*To whom correspondence should be addressed. Fax: 06221 596163.

(magnesium-stabilized beta-alumina) powders from ABB Hochenergiebatterie GmbH, Heidelberg, Germany, that had been prepared from the raw materials Al_2O_3, Na_2CO_3 and MgO. The raw materials had been mixed previously in the correct ratio to yield the company's proprietary composition after calcination and reaction close to 100% β''-Al_2O_3 phase.[7] The calcined powder was jet milled to obtain a mean particle size of about 1 μm and a maximum particle size of 10 μm.

2.1.2 Suspending medium and dispersing aids
As in the case of zirconia,[1] beta alumina suspensions may be stabilized best using polar-protic solvents, such as alcohols like ethanol or 2-propanol, in combination with appropriate dispersing aids. Different oligomeric or polymeric ionic or polar organic compounds, such as trioxadecanoic acid, (acrylic ester/acrylamide) copolymer and (acrylic acid/acrylic ester) copolymer, were tested as dispersing and charging aids. These are referred to as polyelectrolytes C, B and A, respectively, in the following text. For standard deposition experiments the suspensions were presedimented for 2 to 5 h to remove particles larger than about 5 μm.

2.2 Forming

2.2.1 Reference method dry pressing
Some tubes were taken from the standard ABB Hochenergiebatterie GmbH production process to serve as an internal reference. They were fabricated through dry-pressing of spray-dried powder; isostatic pressing at 150 MPa was used.

2.2.2 Electrophoretic deposition (EPD)
For EPD tests and subsequent investigation, the following standard suspensions were used: 2-propanol with 50 mass% powder and 1% trioxadecanoic acid. EPD conditions were: voltage from 80 to 600 V, electric field strength of 40 to 500 V cm^{-1}, current of 5 to 40 mA, current density typically from 0·08 to 0·3 mA cm^{-2}, maximal values tested up to 1·5 mA cm^{-2}, specific conductivity of suspensions of 5 to 10 μS cm^{-1}.

2.3 Drying and sintering
As no dispersants with inherent binder functions could be used in the case of beta-alumina, the drying process had to be more controlled than with zirconia ceramics.[1] Long beta-alumina tubes (300 mm) had to be dried in two steps: predried for 5 to 15 min at ambient conditions inside the deposition apparatus (opening downside, 1 to 2 cm above the table surface) until separation of the bodies from the electrode occurred; final drying at

60°C in a controlled oven (explosion protected, no ventilation) for 30 to 45 min.

Firing at ambient atmosphere in electrically heated furnaces[1] was applied, with maximum temperatures for densification ranging from 1620 to 1640°C (heating rate 5°C min^{-1}, holding time 15 min). In order to prevent sodium losses, the beta-alumina components were covered by an α-Al_2O_3 crucible, the inside of which was clad with platinum foil, or under comparably inert conditions. All beta-alumina components, green or fired ones, were stored at ambient temperature under flowing dry nitrogen.

2.4 Quality assurance and characterization methods
The surface roughness of sintered bodies was measured with the help of a Hommel tester (Hommel-Tester P1, Hommelwerke, VS-Schwenningen, Germany) resulting in two-dimensional surface profiles with a resolution of 10 nm.

Geometrical control of beta-alumina tubes was performed using tools from ABB Hochenergiebatterie GmbH. Besides the wall-thickness, especially the diameter of the sintered tubes was controlled circumferentially at three different positions, namely at the closed end, in the middle and at the open end (using an automatic laser-based system; the same used for the company's standard in-line process quality control procedure).

The ionic resistivity was measured with tube cutoffs of 80 mm length; end faces were graphite coated; measuring frequency was 1 MHz; test measuring temperature was 350°C. These tests were sufficient for the comparison of the resistivity levels of dry-pressed and electrophoretically formed components within the scope of this paper (cf. Ref. 7 and references therein).

3 Results and Discussion

3.1 Powders and powder processing

3.1.1 Viscosity
The influence of different dispersing agents on the viscosity of a beta-alumina suspension is given in Fig. 1. With appropriate dispersing agents (electrolyte C–3,6,9-trioxadecanoic acid), the 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 dispersing agent. Polymer B [(acrylic ester/acrylamide) copolymer] leads to suspensions with intermediate stability. The viscosity decreases with increasing admixture of dispersing agent, but the decrease is not nearly as fast as with electrolyte C and not as
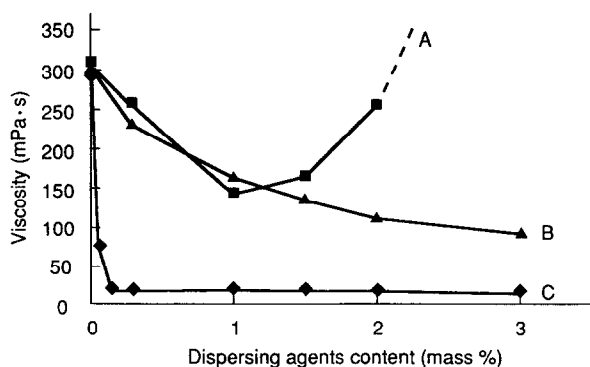
Fig. 1. Influence of three different dispersing agents (polyelectrolytes A, B, C; cf. text) on viscosity of a beta-alumina suspension (70 mass% of powder in 2-propanol; addition of dispersing agents is given in mass% relative to powder mass in a suspension; shear rate $200\,s^{-1}$).

effective. Polyelectrolyte A [(acrylic acid/acrylic ester) copolymer] only shows reduced efficiency in the very restricted range of contents of dispersing agent between 1 and 1·5 mass%.

Dispersing aids with an inherent binding effect would have been preferred so that addition of special binders for increased green strength of the consolidated bodies could have been avoided.[1] But for beta-alumina suspensions, dispersing aids with very effective binding performance could not be found due to the very basic nature of these suspensions. It was found, however, that atmospheric humidity had some strengthening effect through the adherence of powder particles via sodium hydroxide formation at powder particle surfaces.

With the most effective dispersant (electrolyte C), the solids content may be increased to 75 mass% (48 vol%) with still acceptable thinly flowing and pourable suspensions (see Fig. 2).

3.1.2 Particle size distribution

Figure 3 shows the particle size distribution of beta-alumina powder in 2-propanol (with 3,6,9-trioxadecanoic acid as dispersant) as an unfractionated suspension and after two stages of
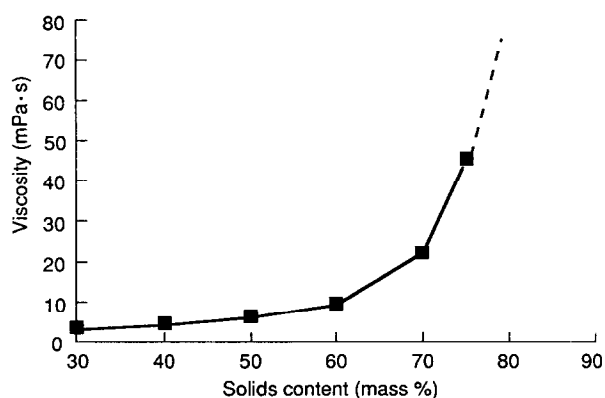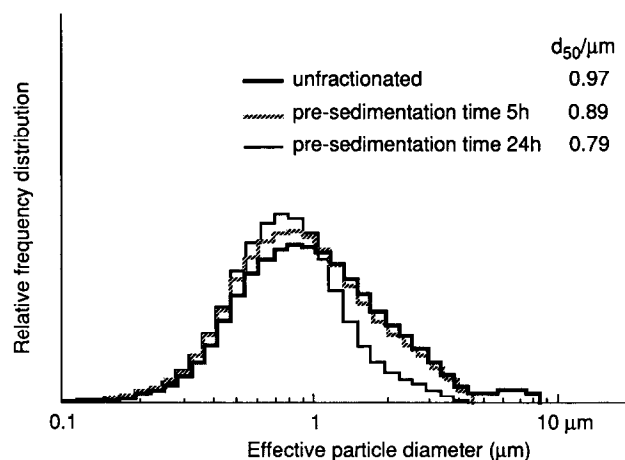

Fig. 3. Particle size distribution of beta-alumina powder in 2-propanol (dispersing aid 3,6,9-trioxadecanoic acid) as unfractionated suspension and after two stages of pre-sedimentation.

pre-sedimentation. Sedimentation and separation of the coarser particles clearly reduce the ratio of oversized powder particles without further affecting the shape of the distribution curves.

3.2 Electrophoretic deposition (EPD)

Figure 4 shows the deposition rate for the EPD of beta-alumina against current density for different solids contents. Deposition rates are 0·5 to $1·0\,mm\,min^{-1}$ for typical experimental conditions (50 mass% powder, 80 to $300\,\mu A\,cm^{-2}$ current density). Higher deposition rates of up to $10\,mm\,min^{-1}$ can be achieved easily for higher solids contents and higher current densities.

3.3 Characterization of deposited, dried and sintered bodies

Sizes of the deposited green tubes were 100 to 300 mm length, 30 to 35 mm diameter and 2 mm wall thickness. Sintered beta-alumina tubes are shown in Fig. 5.
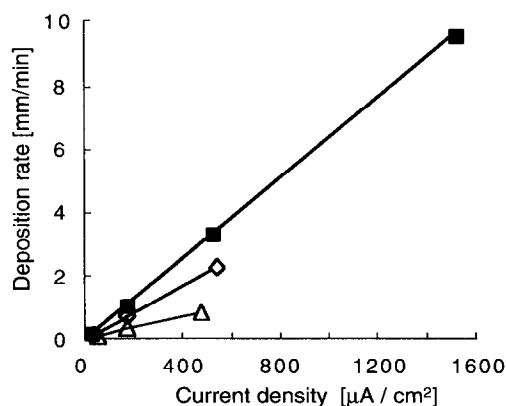

Fig. 2. Influence of solids content on viscosity of beta-alumina suspensions [solvent: 2-propanol, 1 mass% 3,6,9-trioxadecanoic acid (relative to powder mass); shear rate $200\,s^{-1}$].

Fig. 4. Deposition rate for the electrophoretic deposition of beta-alumina powder in 2-propanol with 1 mass% of 3,6,9-trioxadecanoic acid as dispersant against current density for three different solids contents (■: 36·0 vol.%/70 mass%; ◇: 19·5 vol.%/50 mass%; △: 5·7 vol.%/20 mass%).

Dry-pressing: rm-value= 6.29 μm

Roughness (μm)

Measuring length (mm)

Electrophoresis: rm-value= 0.53 μm

Roughness (μm)

Measuring length (mm)

Fig. 6. Surface roughness of an electrophoretically shaped beta-alumina tube in comparison to that of a dry-pressed tube.
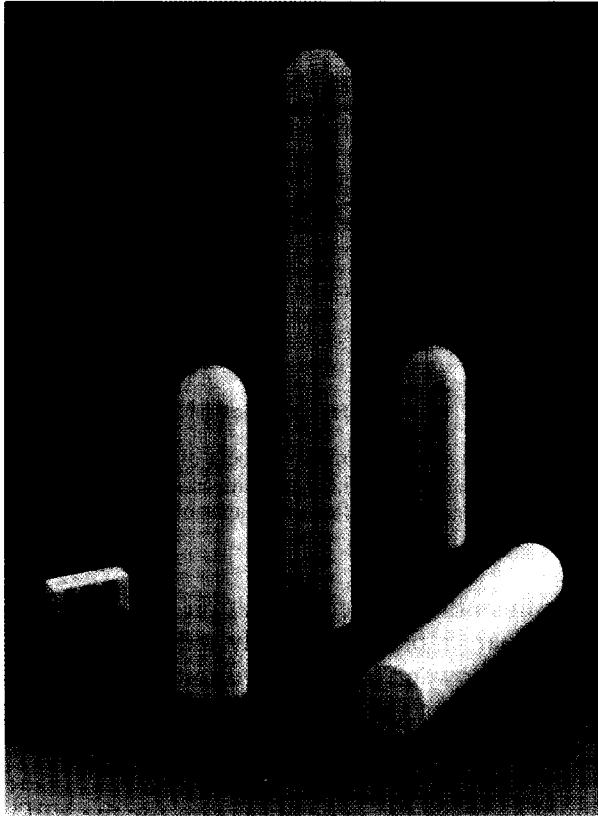
Fig. 5. Electrophoretically produced and sintered beta-alumina tubes (sugar lump dimensions $34 \times 10 \times 16\,mm^3$ length/width/height).

3.3.1 Density, microstructure, phase content, conductivity and surface quality

The green density of electrophoretically shaped bodies is 56·5% ($1\cdot85\,g\,cm^{-3}$), fired densities are 99·4% ($3\cdot25\,g\,cm^{-3}$). The mean grain size of fired components is $3\,\mu m$, when fired at 1620°C—without any exaggerated grain growth. The microstructure of electrophoretically shaped tubes is more homogeneous than the microstructure of dry-pressed tubes which show some tendency to exaggerated grain growth. The phase content of electrophoretically and dry-pressed samples is identical, as the same powder source and firing conditions were used.

The electrical conductivities of the samples tested ($3\cdot7\ldots4\cdot4\,\Omega\,cm$ at 350°C) did not differ from the conductivities of dry-pressed samples from the same powder source when fired under identical conditions. This is not surprising because they were of the same chemical and phase composition, and general microstructure after sintering was comparable.

Figure 6 shows the surface roughness of an electrophoretically shaped beta-alumina tube in comparison to that of a dry-pressed tube. As the achieved level of improvement of ceramic quality cannot be quantified significantly by average values, the surface roughness measurements have been analysed as roughness dynamic or maximum
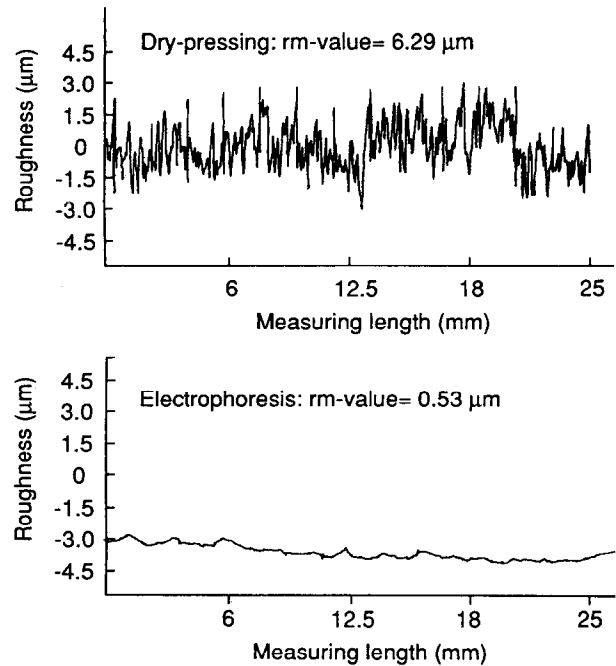
roughness *rm*, i.e. vertical distance between highest and lowest point of the roughness profiles measured along a 25 mm length of the tube surfaces. In the case of an electrophoretically shaped tube, *rm* is 12 times smaller than in the case of a dry-pressed tube ($0\cdot53\,\mu m$ against $6\cdot3\,\mu m$).

3.3.2 Homogeneity and strength

Figure 7 shows strength data for beta-alumina tubes, which had been either dry pressed from spray-dried powder or electrophoretically shaped from stable suspensions without sieving or electrophoretically shaped from stable suspensions with additional sieving of the suspension prior to filling
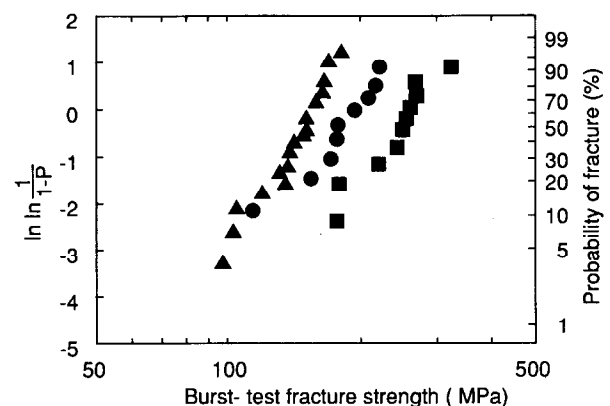
$\ln \ln \frac{1}{1-P}$

Probability of fracture (%)

Burst- test fracture strength (MPa)

Fig. 7. Strength data (internal pressurization) for beta-alumina tubes originating from different manufacturing processes [▲: dry pressed from spray-dried powder ($\sigma_c = 175\,MPa$; m = 9); ●: electrophoretically shaped from stable suspensions in open vessel, unsieved ($\sigma_c = 200\,MPa$; m = 7); ■: electrophoretically shaped from sieved stable suspensions in cleansed & closed vessel ($\sigma_c = 260\,MPa$; m = 7); P = probability of fracture].

it into the 'cleansed & closed' consolidation compartment. Highest strengths were achieved from sieved stable suspensions filled into a 'cleansed & closed' apparatus ($\sigma_c = 260$ MPa) versus 200 MPa for electrophoretic shaping from stable suspensions without further treatment and 175 MPa for conventionally dry-pressed tubes.

For the wet-processed samples without additional sieving and cleansing, fracture origins of 10 (out of 11) samples were within the bulk. For those samples processed with additional sieving and cleansing, fracture origins of 8 (out of 10) samples were at the outer surface (electrode side).

Fractographic analysis showed that sizes of the fracture origins of the tested electrophoretically shaped tubes, even when prepared under sieved and cleansed conditions, are still substantially larger ($60 \mu m$) than the mesh size of the sieve used ($20 \mu m$). In contrast to the results with zirconia suspensions,[1] all cleansing efforts could not reduce the fracture size closer to the mesh size.

Fracture origins larger than the mesh size could have developed during drying or firing as a consequence of reagglomeration after sieving or residual agglomerates,[8,9] perhaps intensified by the micaceous morphology of the beta-alumina powder used. In order to check further whether the typical fracture originating flaws had developed during sintering, additional strength tests were performed with 'semi-fired' tubes (fired at 1400°C). The fracture origins of these tubes showed no significant difference of size and appearance against the fracture origins of fully fired tubes. Therefore it can be concluded that firing (at least above 1400°C) had no significant influence on flaw size. Fracture origins may still come from the powder itself, e.g. from residual agglomerates or from reagglomeration. This was not tested further.

4 Electrophoresis as an Industrial Deposition Process

Before this novel electrophoretic deposition process can be introduced into an industrial production environment, three further quality criteria—beyond materials quality—must be checked, namely reproducibility, production time and cost.

4.1 Reproducibility

In order to be able to check the reproducibility of the electrophoretic deposition conditions, deposition electrodes were manufactured with dimensions that were based on the known shrinkage parameter of 17·2% of the selected powder charge and suspension. Target dimensions of beta-alumina tubes are 25 cm length and 25·64 mm outer diameter

according to the standards for the electrolyte ceramics for the sodium–sulfur high-energy battery of ABB Hochenergiebatterie GmbH. Fifteen tubes were produced under standard conditions (see above), from which 13 whole tubes were obtained after firing. For 10 of these tubes, maximum and minimum values of the diameter readings at the selected three control positions are displayed in Fig. 8. Except for three open end readings, all the values are within the required tolerance width of $\Delta = \pm 0.18$ mm.

4.2 Multiple apparatus

A basic process variable that is critical for any process cost estimate is process time or throughput time. Serial production of single tubes through wet electrophoretic consolidation, as discussed hitherto, can never be an economic process. But the electrophoretic deposition process easily allows parallel production.

The applicability of the colloidal electrophoretic deposition process to parallel or multiple production, therefore, was checked in a first step with a custom-made apparatus that allowed the deposition of five long (25 cm) tubes at a time. A principal drawing of this apparatus is shown in Fig. 9. The hollow electrodes have been mounted into a rig that allows the electrodes to be turned upside down as well as to be moved up and down.

The apparatus is filled through a central filling tube with the tubular electrodes in their starting position (closed end downwards). After electrophoretic deposition has then arrived at the desired wall thickness, voltage is switched off and the whole apparatus is turned by 180°, so that the residual suspension may flow out of the deposition compartments. The apparatus is turned backwards and the filling head and the counter electrodes are removed. The apparatus is turned again, so that
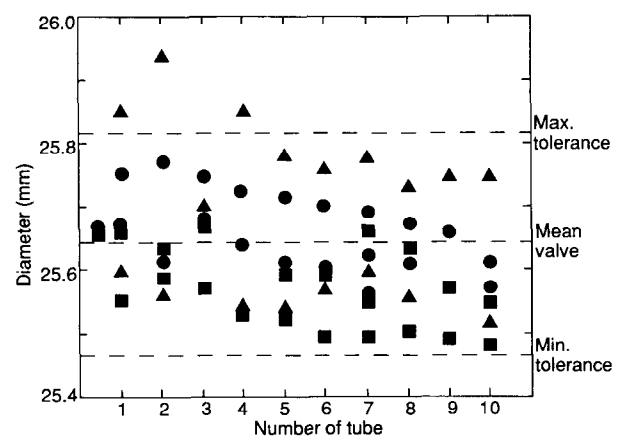

Fig. 8. Maximum and minimum values of the diameter readings of electrophoretically consolidated beta-alumina tubes at three selected control positions (■: closed cap; ●: center; ▲: open end).
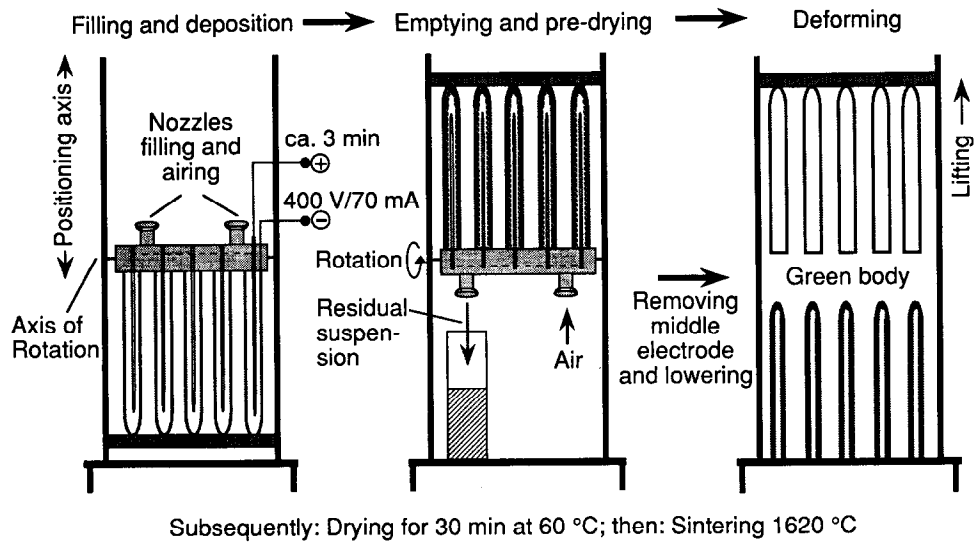
Fig. 9. Schematic drawing of the multiple deposition apparatus showing the three main production steps, filling/forming, emptying/ pre-drying, deforming.

the consolidated body may slip out of the electrode compartment towards the table top (approximately 1 to 2 cm below) while drying. The deposited green bodies are allowed to dry at room temperature for 15 min, then are dried at 60°C for another 30 min, before the apparatus is slowly moved upwards, with the dried green bodies gliding out of the hollow electrodes.

First tests of the multiple deposition apparatus were done at deposition voltages between 400 and 500 V (equivalent to electric field strengths between 400 and $500 \, V \, cm^{-1}$; deposition currents of 70 to 80 mA). The deposition time was 3 to 5 min. Fig. 10 shows the multiple deposition apparatus just before the end of the deforming step and a first

series of deposited dried green bodies outside the apparatus.

4.3 Cost

To check whether further investigations of this new method are justified, a first rough cost comparison was made. Assuming the production of 14 million tubes over 12 years, the investment cost plus material, energy and labor costs were estimated. The estimate was done for three different shaping methods: electrophoretic deposition from fine stable suspensions (e.g. using 5 parallel 20-tube multiple deposition apparatus), large-series isostatic dry-pressing and slip casting. An 85% yield of the production process were assumed for all
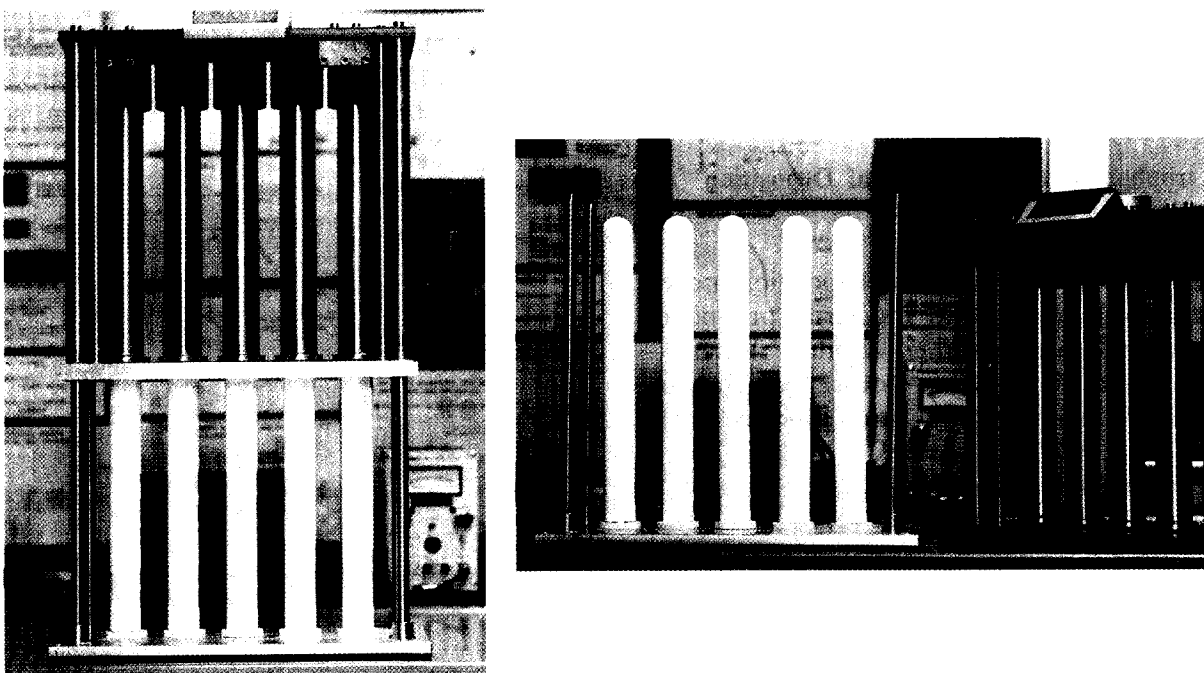

Fig. 10. Photography of the multiple deposition apparatus just before the end of the deforming step and a first series of deposited dried green bodies outside the apparatus.

three processes. This comparison showed[10] that, in addition to its quality advantages, EPD could also become economically competitive.

EPD is semi-fast, but parallel multi-deposition is easy to achieve. Energy requirements for electrophoretic deposition are low, as it is only 2 kWh per 1000 kg of solids for the above deposition rates and current densities. This is substantially lower than the energy requirement for pressure-assisted shaping methods. Dry-pressing is fast and does not need a drying step, but it requires expensive pressure machinery. Slip casting is lengthy with reduced lifetime of tools. At equal yield, the estimated overall cost per electrophoretically produced tube should, therefore, be equal to the cost per tube for dry-pressing and lower than the cost per tube for slip casting.

5 Summary and Conclusions

Functional ceramics such as beta-aluminas require high microstructural homogeneity. For such ceramics, wet shaping from stabilized suspensions of deagglomerated fine powders is an advantageous means to overcome quality deficiencies inherently connected with hitherto used dry powder pressing or with conventional slip casting or with electrophoretic deposition using non-stabilized suspensions of agglomerated powders.

Electrophoretic deposition (EPD) starting from fine stable powder suspensions is a shaping method which fits the above concept. 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 of the consolidation of alpha alumina components[11] (and other references in Ref. 1) and of zirconia components,[1] the method has now been applied to tubes made from beta-alumina powders, and a first step has been taken to develop it further from a laboratory to an industrial scale. Strengths achieved for beta-alumina samples were less than those for alumina[11] and zirconia[1] samples prepared under comparable conditions. The electrophoretically shaped beta-alumina tubes produced from sieved suspensions had a characteristic strength of 260 MPa and a Weibull modulus m = 7 (calculated from burst-testing of whole tubes) against 175 MPa and m = 9 for dry-pressed tubes.

A multiple deposition apparatus, which allows the deposition of five tubes at a time, has been developed and was tested with beta-alumina. A rough first-estimate cost comparison for EPD with other forming methods was based on these results and showed that the EPD from fine stable powder suspensions has the potential to become competitive for industrial-scale manufacturing at better quality.

References

1. Harbach, F. and Nienburg, H., Homogeneous functional ceramic components through electrophoretic deposition from colloidal suspensions—I. Basic concepts and application to zirconia. *J. Eur. Ceram. Soc.*, 1998, **18**, 675–683.
2. Fally, J., Lasne, C., Lazennec, Y., LeCars, Y. and Margotin, P., Study of a beta-alumina electrolyte for sodium sulfur battery. *J. Electrochem. Soc.*, 1973, **120**(10), 1296–1298.
3. Powers, R. W., The electrophoretic forming of beta-alumina ceramics. *J. Electrochem. Soc.*, 1975, **122**(4), 490–500.
4. Powers, R. W., Ceramic aspects of forming beta alumina by electrophoretic deposition. *Am. Ceram. Soc. Bull.*, 1986, **65**(9), 1270–1277.
5. Heavens, S. N., Manufacture of β-alumina shapes by electrophoretic deposition. In *British Ceramic Proceedings, No. 38, Novel Ceramic Fabrication Processes and Applications*, ed. R. W. Davidge. The Institute of Ceramics, Shelton, Stoke-on-Trent, 1986, pp. 119–126.
6. 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, NJ, 1990, pp. 255–283.
7. Harbach, F., Sodium beta"-alumina ceramics: compositions, phases, conductivities. *Silicates Industriels*, 1986, **1986**(5–6), 81–85.
8. Lange, F. F., Metcalf, M., Davis, B. I. and Aksay, I. A., Processing-related fracture origins: I, II, III. *J. Am. Ceram. Soc.*, 1983, **66**(6), 396–398, 398–406, 407–408.
9. Harbach, F. and Weiler, L., Microstructural inhomogeneities—causes and means of control. *cfi/Ber. DKG*, 1986, **63**(3), 107 (part 1); (6), 305–310 (part 2); (7/8), 406–409 (part 3).
10. 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)*. Final report 03 M 2711 8, Bundesministerium für Forschung und Technologie (BMFT)—Materialforschung, Bonn, Germany, 1993 (publicly available at TIB Hannover, Germany, under position number F 95 B719 + a).

11. Harbach, F., Neeff, R., Nienburg, H. and Weiler, L.,
    Homogeneous ceramic components from colloidal suspen-
    sions. In *Ceramic Powder Processing Science, Proceedings*
    of the Second International Conference, ed. H. Hausner,
    G. L. Messing and S. Hirano. 1988. Deutsche Keramische
    Gesellschaft, Köln, Germany, 1989, pp. 609–616.