Available online at www.sciencedirect.com

SCIENCE DIRECT®

Journal of the European Ceramic Society 24 (2004) 3219–3225

www.elsevier.com/locate/jeurceramsoc

Multi-phase ceramics by computer-controlled pressure filtration

A. Mattern*, R. Oberacker, M.J. Hoffmann

Universität Karlsruhe, Institut fur Keramik im Maschinenbau—Zentrallaboratorium, Haid-und-Neu-Str. 7, D-76131 Karlsruhe, Germany

Received 20 June 2003; received in revised form 9 October 2003; accepted 16 October 2003

Abstract

A novel apparatus for computer controlled pressure filtration has been constructed. With it, the precise flow rate of multiple ceramic suspensions of different compositions can be controlled. Suspensions are mixed before entering the filtration chamber. By dynamically adjusting the different flow rates, mixed compositions anywhere between 100% composition A to 100% composition B can be realised as a function of the filter cake height. This is suitable for producing e.g. functionally graded materials or layered structures. This has been demonstrated for alumina–zirconia composites. The process is suitable for all materials that can be handled by slip casting.

Keywords: Composites; Graded/layered microstructure; Shaping; Slip casting; Suspensions

1. Introduction

Pressure slip casting is a forming technique for ceramic parts with complex shapes that cannot be fabricated by dry pressing. It has long been established in the traditional clay based ceramic industry as an economical replacement for slip casting in plaster of paris moulds.[1–6] More recent work has been undertaken to use pressure slip casting for the fabrication of technical ceramics where it has also become a reliable forming technique for materials such as silicon nitride[5,7–10] and zirconia.[11] The usual goal when producing parts with pressure filtration is to achieve a green body of homogeneous composition and density, which can be problematic if segregation effects occur or if a slightly agglomerated suspension is used, which will lead to a compressible filter cake,[12,13] where even the high pressures used in filter presses are not enough to force a homogeneous packing throughout the cake. Advances have been made in extending the capabilities of filter presses to get more accurate and on-line information about cake formation and filtration behaviour of suspensions.[14] Approaches taken to study cake formation in slip cast ceramics using ultrasonics[15,16] should be applicable to pressure slip casting as well.

A common factor of these works is that the slurry composition is not changed during the process and that a green body with a fixed composition is produced. Traditional slip casting on plaster of paris moulds on the other hand has long and successfully been used to produce composite ceramics by sequentially casting slips of different compositions. With this method, layers of varying composition are manually cast consecutively with the driving force provided by the capillary suction of the porous mould to achieve layered or functionally graded samples. If the cast layers are thin enough and the composition difference between layers is small, quasi-continuously graded materials can be achieved. In this article layered structures will denote well-defined layers with steep changes of composition whereas gradients will refer to continuous or quasi-continuous change of composition with smooth transitions.

Among others, work has been reported on layered alumina–zirconia composites,[17] graded alumina–zirconia materials,[18,19] layered silicon carbide–graphite composites,[20] alumina–aluminum titanate gradients,[21] layered β-sialon-$S1_3N_4$ composites,[22] zirconia–stainless steel[23,24] and zirconia–nickel gradients.[25]

Steps towards the automation of the mixing process and the filtration have been proposed.[26,27] Computer controlled pumps were used to pump specified amounts

---

* Corresponding author. Tel./fax: +49-721-608-4246.
E-mail address: andreas.mattern@ikm.uni-karlsruhe.de (A. Mattern).

0955-2219/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2003.10.037

of suspensions of different composition through a mixer before they entered and passed through a porous mould before being collected. Alumina–zirconia gradients from 100% alumina to 60% alumina/40% zirconia have been reported. The pumps used in this setup provided the necessary flow of the suspensions through the mixer as well as the interior of the pipe-shaped mould, but the driving force of the actual filtration was the capillary suction of the porous mould. Studies of cake formation kinetics depending on slurry composition as well as previously deposited filter cake layers were necessary to control the flow rate required to achieve the desired gradient profile. Due to the large volume of the mould as well as the flow profile inside of it, no sharp changes in slurry composition for the realization of layered structures were possible with this setup.

A further process for the production of hydroxyapatite materials with a continuous porosity gradient has been reported[28] where a suspension containing a pore forming agent was continuously fed into a tank. Here, a vacuum pump provided the driving force for the filtration process and again only a continuous gradient was possible due to the mixing of the suspensions in the tank. A problem reported was the sedimentation of the particles of different size and density because of the slow cake formation rate with the driving pressure limited to one atmosphere. The same holds true for the setups using capillary suction as the driving force which limits the maximum thickness of the parts and the composition of the suspensions.

The first processing route for producing graded materials by automated pressure filtration has been proposed.[29,30] In this work computer controlled mixing of two suspensions was done inside of a pressure vessel where the filtration was driven by gas pressure. Cake formation rate and thus layer thickness was driven by controlling the pressure applied. It was necessary to obtain detailed parameters of cake porosity and permeability. This allowed a modelling of the pressure cycle to achieve the desired deposition rates. In practice, problems arose with sealing the large pressure vessel for the desired pressures of up to 10 MPa.[31] Another problem was the solubility of the gas under high pressure which led to bubble formation inside of the green compact when the pressure was dropped to ambient.

The work presented in this article is a new and extended version of that process. It is a combination of the versatility of the slip stacking process used on plaster of paris moulds with the precision and speed of deposition of computer controlled pressure filtration. Commercial high pressure metering pumps were used to drive the filtration process and control the relative flow rates of the suspensions mixed in a static mixer to achieve the desired cake structure. Modelling and controlling of the process was greatly simplified with this approach due to the volumetric pumping.

Previously, this process had practically not been feasible due to the abrasive nature of the ceramic suspension. This problem has been overcome by indirect pumping: only pure water is pumped and flows into pressure vessels with an internal, non-permeable membrane. One side of the vessel is filled with the desired suspensions and water is pumped into the other compartment. The water flowing into the vessels replaces the same volume of suspension which is then mixed and deposited.

2. Theorectical background

Pressure slip casting and filter pressing are forming techniques in which particulate suspensions are consolidated by dewatering. The suspension is filtered at the interface of a porous filter medium. The driving force is provided either by applied gas pressure or liquid pressure provided by a pump or filter press.

The cake growth rate $\mathrm{d}h/\mathrm{d}t$ can be described using Darcy's Law with the basic equation of cake filtration:

$$\frac{\mathrm{d}h}{\mathrm{d}t} = \frac{\dfrac{c_\mathrm{s}}{c_\mathrm{c}-c_\mathrm{s}} \cdot \Delta p}{\eta\left(\dfrac{h}{D} + R_\mathrm{M}\right)} \tag{1}$$

where h represents the filter cake height, t the filtration time, Δp the filtration pressure, c_s and c_c the solids loading of the suspension and the cake, η the filtrate viscosity, D the specific cake permeability and R_M the flow resistance of the filter medium.

Well stabilised ceramic suspensions form incompressible filter cakes that have a flow resistance several orders of magnitude greater than that of the filter medium which can be neglected for further calculations.

This equation is well understood. For homogenous suspensions it can be integrated for the typical cases of constant pressure or constant flow rate. For suspensions with varying composition the case becomes much more complicated as the solids loading of the cake and the permeability are functions of the composition and thus vary with the cake height. As a consequence, for processes that are controlled by the pressure applied or deposition time at a constant pressure, the cake formation rate becomes dependent on the cake that has been previously deposited.[27,29]

This work uses a volumetric approach where metering pumps supply a precisely controlled volume flow of the suspension independent of the cake permeability. The buildup of the pressure to sustain the desired flow rate is the response of the system and not the controlling factor for the formation rate like in the previous. Assuming that no solid passes the filter, a mass balance for a pumped volume unit of suspension $\mathrm{d}V_s$ deposited on the filter gives a corresponding volume of filter cake $\mathrm{d}V_c$:

$$\mathrm{d}V_c = \frac{c_s}{c_c}\mathrm{d}V_s \tag{2}$$

With a constant filter area A this gives a height increase $\mathrm{d}h$ of the cake of

$$\mathrm{d}h = \frac{1}{A}\frac{c_s}{c_c}\mathrm{d}V_s \tag{3}$$

If two suspensions containing solid phases α and β at equal volume loading c_s are mixed before depositing a layer $\mathrm{d}h_{\alpha\beta}$ it can be expressed as

$$\mathrm{d}h_{\alpha\beta} = \frac{1}{A}\frac{c_s}{c_{\alpha\beta}}\mathrm{d}V_{s,\alpha}\mathrm{d}V_{s,\beta} \tag{4}$$

with a cake solids loading $c_{\alpha\beta}$ depending on the composition. If the particles of solids phase α and β are of similar shape and size, this will be equal to the cake solids loading c_c. For a bimodal size distributions $c_{\alpha\beta}$ has to be calculated or determined experimentally as shown in Ref. 30.

If no axial mixing occurs in the piping, this approach can be used to vary the cake composition by changing the flow rates of the starting suspensions. Layers of a predetermined thickness and ratio of phase α and β can be deposited consecutively on top of each other which allows the manufacturing of layered or graded structures. Flow rates can be varied continuously so that completely smooth graded structures can be achieved.

Contrary to earlier approaches this deposition is independent of the previously deposited filter cake as long as the resulting pressure buildup is within the limits of the metering pumps. Steep changes of composition with sharp interface layers can be achieved. This was impossible with earlier automated approaches and only possible with manually slip casting layers and waiting for previous layers to dry.

The present method is suitable for mixing more than two suspensions and theoretically any number of phases could be deposited with this approach as long as the mixed suspension is stable and the compact can be sintered. For practical purposes, the experimental setup has been limited to two solids phases for the present.

3. Experimental verification

3.1. Setup

Fig. 1 shows the experimental setup. Two commercial metering pumps controlled by a PC were used. The pumps were LEWA Modular diaphragm pumps supplied by Herbert Ott GmbH (Leonberg, Germany). Flow rate could be precisely controlled and was almost independent of pressure as can be seen in Fig. 2. Maximum flow rate dropped by 10% when pumping against a pressure of 10 MPa as compared to pumping against ambient. The flow rate at 5 MPa was used as a basis for processing the samples presented in this report. A schematic characteristic curve of a rotary pump is included in Fig. 2 to show the difference between this type of pump and the metering pumps used.

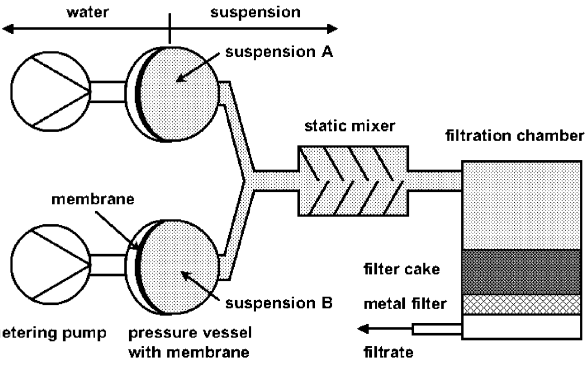

Fig. 1. Experimental setup of the computer controlled pressure filtration apparatus.

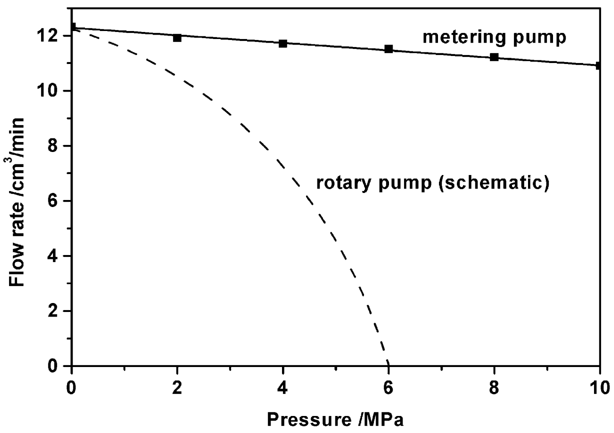

Fig. 2. Flow rate of the metering pumps (measured) compared to that of a rotary pump (schematic) depending on the pressure.

Due to the abrasive nature of ceramic slips it is not possible to pump them directly with metering pumps. Pump types such as rotary pumps that are less susceptible to abrasion have a flow rate which is highly dependent on pressure and suspension viscosity and can thus not be used for metering. Tube pumps are resistant to abrasion as no moving parts are in contact with the liquid and they can be used for metering to some extent, but cannot supply pressures above 1 MPa, which is inadequate for the high cake resistances of technical ceramics.

To overcome this problem, an indirect approach was used. The metering pumps used water as a medium which they pumped into stainless steel pressure vessels with an internal, non-permeable membrane. They were built from commercially available diaphragm accumulators which were filled with the slips that were to be processed. Water entering a vessel's inlet displaced the same amount of suspension through the corresponding outlet. High pressure hoses connected the two vessels to a static mixer. The mixer was a KM-type Kenics static mixer by Chemineer Inc. (Dayton, Ohio, USA) tailored to the flow rates and viscosities of the suspensions. The mixed suspensions entered a filtration chamber with a sinter metal filter onto which the filter cake was deposited.

The whole setup was filled with water by a small secondary pump before the experiment to keep unwanted air bubbles out of the slips. Tests with clear tubes showed a clear suspension front with negligible dilution by the water. Slips of white alumina and a black alumina/carbon mixture pumped consecutively showed plug-flow behaviour with no axial mixing allowing steep changes of composition with sharp interfaces between layers.

The setup was fitted with an electronic pressure transducer connected to the PC which also measured and recorded the filtrate flow. Safety release valves with an adjustable opening threshold between 5 and 12 MPa were fitted to the piping between the metering pumps and the pressure vessels. Aside from the safety aspect, these allowed conducting constant pressure filtration experiments to measure cake permeabilities for homogeneous compositions.

4. Materials and processing

Alumina and zirconia were chosen as the substances with which to demonstrate the feasability of the process. Both powders can easily be dispersed in water and suspensions can be mixed at any ratio. Alumina Alcoa CT3000SG and zirconia Tosoh TZ-3Y were used as starting powders. Separate suspensions of each powder with a solids loading of 10% were made. The powders were dispersed with Dolapix CE 64 (Zschimmer & Schwarz, Lahnstein, Germany) and attrition milled for one hour. The zirconia had a mean particle size of $x_{50}=0.45$ μm, the alumina of $x_{50}=0.74$ μm. Sedimentation experiments showed that the slips were stable for several hours with no measurable segregation so no sedimentation effects were expected during the pressure filtration process. The cake solids loading of approx. 65 Vol.% was relatively independent of the powder mixture because of the similar size and shape of the starting powders.

A control program on the PC was used to control the pumps and thus the mixing and filtration of the separate suspensions. It also collected the experimental data for flow rate and pressure. Based on measurements on homogeneous filter cakes without gradients it was possible to obtain samples with continuous linear and hyperbolic alumina–zirconia gradients. Deposition time for a 10 mm thick sample was found to be 30 min with a final pressure of 9 MPa. Thicker structures are possible within the pressure limit of 10 MPa of the metering pumps employed if a slower cake formation rate is chosen. After deposition the resulting green bodies were dried in two stages to prevent cracking. First they were dried for 24 h at 20 °C and 90% relative humidity and then for 24 h at 80 °C. Samples were sintered at 1550 °C in air for 1 h. After cutting and polishing they were thermally etched at 1350 °C for microstructural charaterization using an SEM (Leica Stereoscan 440).

5. Results and discussion

5.1. Microstructure

Sintered samples showed no cracking or macroscopic pores. The zirconia-rich side was densified more and had a higher shrinkage than the alumina-rich one, resulting in a slight macroscopic deformation. Micro-

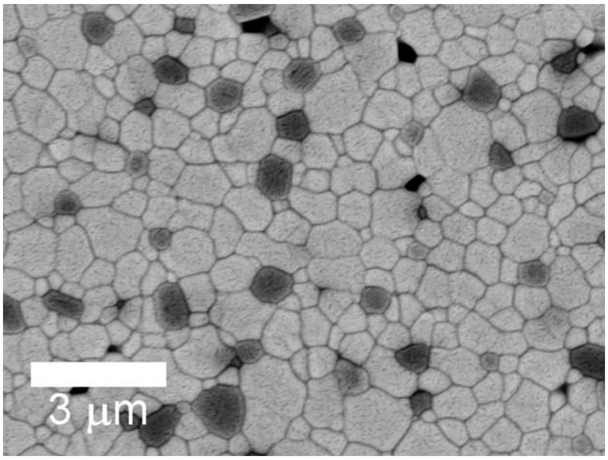

Fig. 3. Microstructure of the ziconia-rich side of a graded sample.

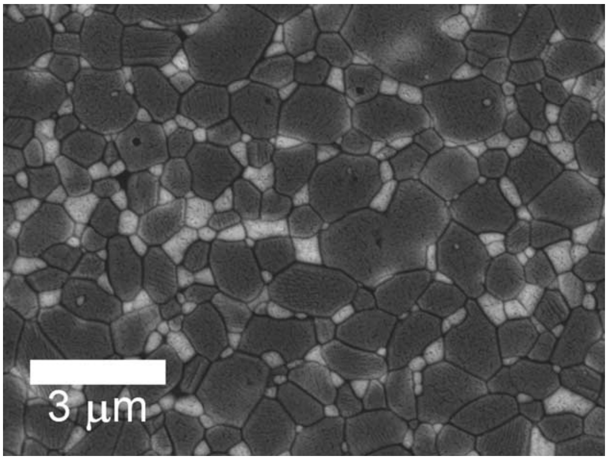

Fig. 4. Microstructure of the alumina-rich side of a graded sample.

pores of a size similar to the grains were found throughout the material which has been reported for homogeneous composites of the materials.[32] Total density was greater than 95%. The microstructure at the zirconia-rich and the alumina-rich side of a disk with a linear gradient in composition and with a thickness of 10 mm is shown in Figs. 3 and 4. SEM-images were taken in BSE mode showing bright zirconia grains and dark alumina grains.

The different phases are well distributed with no visible agglomeration, indicating that the static mixer employed worked very efficiently in mixing the dispersed suspensions. The zirconia-rich microstructure shows small, intergranular pores, the alumina-rich one shows both inter- and intragranular ones. An increase in grain size is visible towards the single phase sides, which has been reported before.[32] There is a particularly strong grain growth for the alumina grains not surrounded by zirconia.

5.2. Sample gradients

Fig. 5 shows an overview of the sample with a linear gradient in composition with a change from pure zirconia to pure alumina. The sample had a thickness of 10 mm, x denotes the distance from the pure zirconia surface. The images clearly show an increase in the alumina fraction and the increase in grain size for the pure phases when the dispersed second phase grains did not hinder grain growth. The change of composition is very smooth with no visible layers.

A similar analysis was performed for the sample where the composition followed a hyperbolic profile, with a change from pure alumina to almost pure zirconia over a 4 mm thick plate.

Image analysis was performed on the basis of the SEM micrographs taken across the thickness of the samples. The analysis was done using the software analySIS 3.1 (Soft Imaging System, München, Germany).

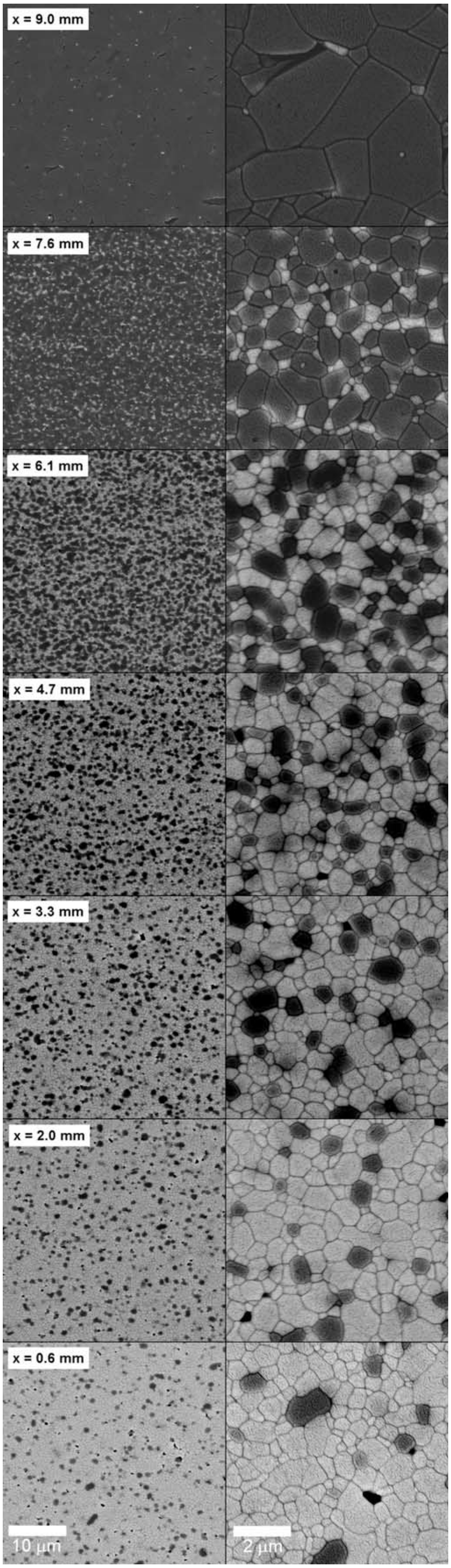

Fig. 5. Linear zirconia-alumina gradient across a sample with 10 mm thickness.

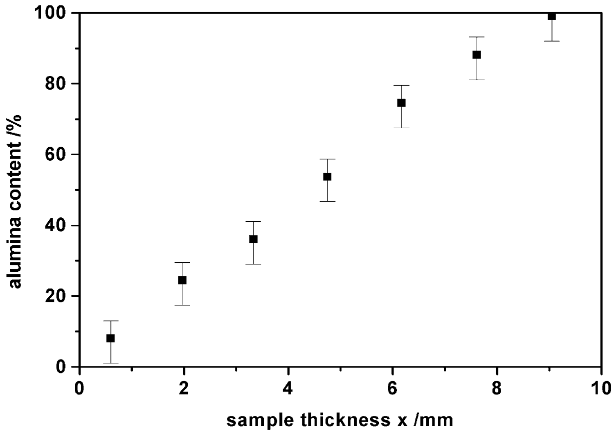

Fig. 6. Alumina-content across the sample measured by image analysis for a linear gradient.

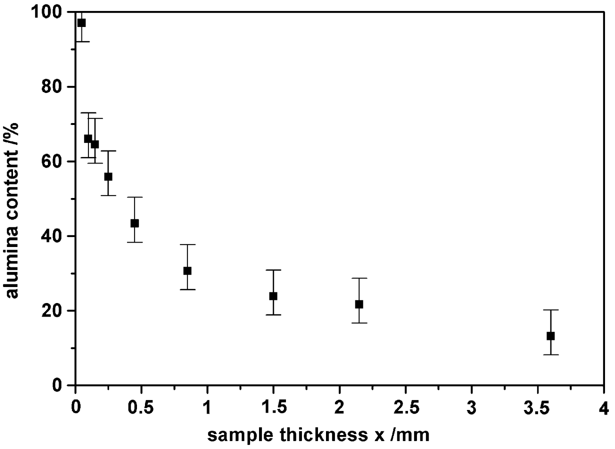

Fig. 7. Alumina-content across the sample measured by image analysis for a hyperbolic gradient.

The strong difference in brightness between alumina and zirconia grains allowed a binarisation of the images which could then be quantified. Pores in the microstructure were counted towards the alumina content as they appeared black on the images, slightly overestimating the alumina content. Fig. 6 shows the results of the analysis for the linear gradient, Fig. 7 for the hyperbolic one. Both the linear and the hyperbolic function were clearly followed.

Layered composites with sharp interfaces are the subject of current investigations which will be presented in the future.

6. Conclusions

A new processing route for multi-phase ceramics through computer controlled pressure filtration has been successfully established. It combines the advantages of pressure filtration with the versatility of traditional slip casting in plaster of paris moulds. A fast deposition rate along with computer controlled precision and very homogeneous mixing can be achieved. Through the use of computer controlled volumetric metering pumps and an indirect pumping approach a wide variety of composites can be made. This has been shown for different smooth gradients with layered structures being under investigation. As long as the individual solids phases can be put into stable suspensions that can be mixed and then sintered together after filtration and drying, any disk-like structure with a predetermined change of composition across the thickness can be achieved. A wide variety of such systems has been reported and successfully produced with traditional slip casting, and some of those will be examined with the setup reported here. The volumetric approach of the process made possible by the indirect pumping approach greatly simplifies modelling and process control compared to previous attempts at modelling and automation of a filtration process with changes of composition in the suspension. This is because the growth rate is independent of the previously deposited structure as long as the pressure resulting from the flow rate stays within the limits of the metering pumps.

The theory and modelling has been validated with zirconia–alumina composites where smooth, linear and hyperbolic changes of composition have been produced. The results have been verified by image analysis of the microstructures across the composition, showing linear and hyperbolic gradients just as the control program was designed to produce. Differences in sintering behaviour leading to stresses in the sample have been compensated by the graded structure, leading to a near-dense body with only a slight curvature due to the higher shrinking of the zirconia-rich side.

References

1. Adcock, D. S. and McDowall, I. C., The Mechanism of Filter Pressing and Slip Casting. *Journal of the American Ceramic Society*, 1957, **40**, 355–362.
2. Fennelly, T. J. and Reed, J. S., Mechanics of Pressure Slip Casting. *Journal of the American Ceramic Society*, 1972, **55**, 264–268.
3. Lange, F. F. and Miller, K. T., Pressure Filtration: Consolidation Kinetics and Mechanics. *American Ceramic Society Bulletin*, 1987, **66**, 1498–1504.
4. Tiller, F. M. and Tsai, Chun-Dar., Theory of Filtration of Ceramics: I, Slip Casting. *Journal of the American Ceramic Society*, 1986, **69**, 882–887.
5. Fries, R. and Rand, B., Slip-Casting and Filter-Pressing. In R. J. Brook, editor, *Materials Science and Technology—A Comprehensive Treatment—Processing of Ceramics Part I,* volume 17A. VCH VerlagsgesellschaftWeinheimmbH, 1996.
6. Klein, G., Druckgieβen keramischer Erzeugnisse. In Wilhelm Bilke, editor, *Handbuch der Keramik,* pages 1–13. Verlag Schmid GmbH, Gruppe 1 D 1.6 (Folge 343) edition, 1997.
7. Kotte, J. F. A. K., Denissen, J. A. M. and Metselaar, R., Pressure Casting of Silicon Nitride. *Journal of the European Ceramic Society*, 1991, **7**, 307–314.
8. Lyckfeldt, O., Lidén, E., Persson, M., Carisson, R. and Apell, P., Progress in the Fabrication of Si3N4 Turbine Rotors by Pressure Slip Casting. *Journal of the European Ceramic Society*, 1994, **14**, 383–395.
9. Oberacker, R., Trendler, A. and Geyer, A., Optimierter Schlickerdruckguß Als Formgebungsverfahren für additivarme Siliziumnitrid Hochtemperaturwerkstoffe. In G. Ziegler, H. Cherdron, W. Hermel, J. Hirsch and H. Kolaska, editors, *Werkstoffwoche '96: Symposium 6: Werkstoff- und Verfahrenstechnik,* pages 551–556, 1997.
10. Moreno, R., Salomoni, A., Stamenkovic, I. and Castanho, S. M., Colloidal Filtration of Silicon Nitride Aqueous Slips, Part II: Slip Casting and Pressure Casting Performance. *Journal of the European Ceramic Society*, 1999, **19**, 49–59.
11. Uchikoshi, T., Sakka, Y., Ozawa, K. and Hiraga, K., Pressure Filtration and Sintering of Fine Zirconia Powder. *Journal of the European Ceramic Society*, 1998, **18**, 669–674.
12. Lin, C.-Y. and Kellett, B. J., General Observations of Constant Flow Rate Filter Pressing. *Journal of the American Ceramic Society*, 1998, **81**, 2093–2108.
13. Biesheuvel, M. P. and Verweij, H., Influence of suspension

concentration on cast formation time in pressure filtration. *Journal of the European Ceramic Society*, 2000, **20**, 835–842.

14. Tarleton, E. S., Using mechatronics technology to assess pressure filtration. *Powder Technology*, 1999, **104**, 121–129.
15. Hutchins, D. A. and Mair, H. D., Ultrasonic monitoring of slip-cast ceramics. *Journal of Materials Science Letters*, 1989, **8**, 1185–1187.
16. Appleton, S., Hutchins, D. A. and Lewis, M. H., Ultrasonic Monitoring of Slip Casting Kinetics of Silicon Nitride Ceramics. *Journal of the European Ceramic Society*, 1991, **8**, 339–344.
17. Requena, J., Moreno, R. and Moya, J. S., Alumina and Alumina/Zirconia Multilayer Composites Obtained by Slip Casting. *Journal of the American Ceramic Society*, 1989, **72**, 1511–1513.
18. Moya, J. S., Sánchez-Herencia, A. J., Requena, J. and Moreno, R., Functionally gradient ceramics by sequential slip casting. *Materials Letters*, 1992, **14**, 333–335.
19. Sánchez-Herencia, A. J., Moreno, R. and Jurado, J. R., Electrical transport properties in zirconia/alumina functionally graded materials. *Journal of the European Ceramic Society*, 2000, **20**, 1611–1620.
20. Zhang, L. and Krstic, V. D., High toughness silicon cabide/graphite laminar composite by slip casting. *Theoretical and Applied Fracture Mechanics*, 1995, **24**, 13–19.
21. Requena, J., Moya, J. S. and Pena, P., A12TiO5–A1203 Functionally Gradient Materials Obtained by Sequential Slip Casting. In J. B. Holt, editor, *Ceramic Transactions 34: Functionally Gradient Materials—Proceedings of the Second International Symposium on Functionally Gradient Materials, San Francisco 1992,* pages 203–210, 1993.
22. Kato, M., Got, Y. and Fukasawa, T., Rheological characterisation of beta-sialon and Si3N4 slips and fabrication of multilayered composites by slip casting. *Journal of Materials Science Letters*, 1997, **16**, 2055–2057.
23. Yamaoka, H., Yuki, M., Tahara, K. and Irisawa, T., Fabrication of Functionally Gradient Material by Slurry Stacking and Sintering Process. In J. B. Holt, editor, *Ceramic Transactions 34: Functionally Gradient Materials—Proceedings of the Second International Symposium on Functionally Gradient Materials, San Francisco 1992,* pages 165-172, 1993.
24. Yung, Y.-G. and Choi, S.-C., Fabrication of 3Y-TZP/SUS3O4 functionally graded materials by slip casting; application of porous alumina molds. *Materials Letters*, 1998, **37**, 312–319.
25. Takebe, H. and Morinaga, K., Fabrication of Zirconia–Nickel Functionally Gradient Materials by Slip Casting and Pressureless-Sintering. *Materials and Manufacturing Processes*, 1994, **9**, 721–733.
26. Marple, B. R. and Boulanger, J., Graded Casting of Materials with Continuous Gradients. *Journal of the American Ceramic Society*, 1994, **77**, 2747–2750.
27. Tuffé, S. and Marple, B. R., Graded Casting: Process Control for Producing Tailored Profiles. *Journal of the American Ceramic Society*, 1995, **78**, 3297–3303.
28. Iwata, M., Shimono, A., Kishiro, K. and Yoshihiko, X., Preparation of Porous Hydroxyapatite Materials with a Continuous Porosity Profile by Use of Filtration Method. *J. Japan Inst. Metals*, 1998, **62**, 1088–1094.
29. Dröschel, M., Oberacker, R. and Hoffmann, M. J., Simulation of a Pressure Filtration Process for Making Porosity Graded Silicon Carbide Evaporation Tubes. In W. A. Kaysser, editor, *Materials Science Forum: Functionally Graded Materials 1998,* volume 308-311, pages 814-820, 1999.
30. Dröschel, M., Hoffmann, M. J., Oberacker, R., Both, H. v., Schaller, W., Yang, Y. Y. and Munz, D., SiC-Ceramics with Tailored Porosity Gradients for Combustion Chambers. *Engineering Ceramics: Multifunctional Properties—New Perspectives, Trans Tech Publications: Key Engineering Materials,* 175–176:149–162, 2000.
31. Kieback, B., Neubrand, A. and Riedel, H., Processing techniques for gradient materials. *Mat. Sci. Eng. A*. (submitted for publication).
32. Rytkönen, T., Keskinen, K. and Lintula, P., Fabrication and Properties of Alumina-Zirconia Composites. In H. Hausner, G. L. Messing and S. Hirano, editors, *Ceramic Powder Processing Science—Proceedings of the Second International Conference, Bertesgaden, Germany,* 1988.