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Pressure slip casting of coarse grain oxide ceramics

Stefan Schafföner *, Christos G. Aneziris

Institute of Ceramic, Glass and Construction Materials, Technische Universität Bergakademie Freiberg, Agricolastrasse 17, 09596 Freiberg, Germany

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Abstract

This contribution investigates the pressure slip casting of large coarse grain oxide ceramic bodies with a water soluble organic additive system. This organic additive system allows the preparation of a stable and pumpable slip containing alumina rich magnesia aluminate spinel of a size of up to 3 mm and an easy demolding of crack free, dimensionally stable bodies with negligible gradients due to sedimentation. Cut out samples of fired bodies are examined on apparent porosity, dynamic elastic modulus, modulus of rupture, and pore size distribution. Computer tomography showed very homogenous and dense bodies. The effects of different maximum grain sizes as well as possible sedimentation and segregation of the slip on the mechanical properties and microstructure are evaluated by using the Student's t-test. The most promising results of this study indicate that it is possible to reproducible fabricate coarse grain ceramics for refractory and other high temperature applications by pressure slip casting.

Keywords: A. Slip Casting; E. Refractories; Pressure slip casting; Coarse grain ceramics; Magnesia aluminate spinel

1. Introduction

The enhancement of ceramic slip casting by external pressure instead of capillary suction, the so called pressure slip casting, is known for over eighty years [1]. Conventional slip casting usually uses porous plaster of Paris molds, which can be used for about 100 times. Due to capillary forces of the pores in the mold the dispersing medium in the slip is absorbed and the cast layer is formed at the interface of the mold with the slip [2]. Slip casting can be considered as a filtration process [3], which is why the buildup of the filtration cake can be accelerated either by vacuum on the mold side or by additional pump pressure on the slip side. Consequently capillary active plaster of Paris molds with a capillary pressure of less than 200 kPa have been replaced by polymeric molds with larger pores because they allow an effective casting pressure of up to 4 and therefore substantially reduce the casting time. In addition, these plastic molds are more durable and can be used for several thousand times [2,4–6].

In general slip casting is a profitable technology for large, hollow shapes of thin to modest wall thicknesses and for the production of complicated, near-net shape bodies of low texturing [2]. Using pressure slip casting even bodies of larger wall thicknesses can be formed in reasonable process times. Moreover it offers the possibility of automation, which is one reason why it is more profitable than conventional slip casting.

Today, pressure slip casting is state of the art for the production of ceramics containing clay minerals such as sanitary ware, cookware and China. Furthermore there has been considerable effort to produce technical ceramics by pressure slip casting [5–8]. However, until recently there has been only little attention paid to the possibility of forming coarse grained ceramics by pressure slip casting.

The adding of coarse grain into the ceramic matrix has several benefits for high temperature applications, such as improving the thermal shock, corrosion, and creep resistance. Besides, the sintering shrinkage is reduced as well. The improvement of the thermal shock resistance results mainly from a microstructure with a microcrack network. This microcrack network can be induced by thermal expansion mismatch of different phases or by a faster sintering of the finer particle fraction than the coarse grain fraction [9,10].

In a previous work Klippel et al. [11] evaluated significant parameters for the pressure slip casting of suspensions with coarse granular grain. In that study a falling ball viscometer has been applied to investigate the rheological behavior of the slips, i.e. thixotropy and rheopexy. Furthermore, they stated the importance of a plug flow of the slip in the tubes during filling

* Corresponding author. Tel.: +49 3731392008.
E-mail address: stefan.schaffoener@ikgb.tu-freiberg.de (S. Schafföner).

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of the mold. A plug flow can be achieved through a moderate filling pressure and an adequate large inner tube diameter, depending on the maximum particle size of the slip. In addition, filtration experiments in a compression permeability filtration (CPF) cell as well as scale up experiments in a commercial pressure slip casting machine were conducted. These scale up experiments had the drawback that it was not possible to demold a dimensionally stable body.

Through modifications of the additive system it was possible to overcome these drawbacks. Thus, the purpose of this study is to describe and evaluate the pressure slip casting of large coarse grain alumina rich magnesium aluminum spinel ceramics by determining microstructure features and mechanical properties.

2. Experimental

2.1. Materials and slip preparation

The current study investigates the preparation and testing of fired samples obtained from two different slips. Both slips contained alumina-rich magnesium aluminate spinel (AR 78, Almatis GmbH, Germany) and a fraction of reactive alumina (MR 70, Martinswerk GmbH, Germany). The Magnesium aluminate spinel was chosen due to its wide use as a refractory material for castables [12]. All the samples were prepared and tested in a random order for the purpose of reducing experimental flaws. The particle size distribution was formulated according to the packing model of particles described in Eq. (1) [13–16].

$$P_i = \frac{d_i^q - d_{\min}^q}{d_{\max}^q - d_{\min}^q} \tag{1}$$

d_i is the particle size of fraction i. $d_{\max}$ and $d_{\min}$ are the maximum and minimum particle size of the mixture. P_i is the cumulative percentage finer than. q is the distribution parameter.

As reported by Klippel et al. [11] the particle size distributions were optimized with a distribution parameter of $q = 0.25$, ensuring a low-thixotropy of the slip. In this study, the maximal grain size of the two slips was 1 mm and 3 mm, respectively, with the intention to estimate the influence of the maximal grain size on the stability of the slips and on other properties of the fired bodies. The quantiles of the particle size distribution of the used ceramic raw materials are listed in Table 1. The particle sizes were determined by sieve analysis according to the standard DIN 66165-2 for the two larges particle fractions and by laser granulometry (Beckman Coulter LS230, Beckman Coulter Inc., USA) according to the standard DIN EN 725-5 for the others.

In order to prevent sedimentation of the coarse grain and provide sufficient green strength after casting, organic additives were admixed. The additive system was adapted from [11], but the added amounts were slightly higher. The addive system consisted of a commercial binder (0.9 wt.%, Optapix AC 170, Zschimmer & Schwarz GmbH & Co KG, Germany), a commercial dispersant (0.025 wt.%, Dolapix CE 64, Zschimmer & Schwarz GmbH & Co KG, Germany), and 0.02 wt.% Xanthan as a stabilizer. According to the manufacturer Optapix AC 170 is a polymer dispersion, whereas Dolapix CE 64 is described as a ammonium polyacrylate solution [17]. All the additves were carefully solved without flocculation in 12 wt.% purified water as the dispersing medium using a Heidolph RZR2102 visco-jet stirrer. Then the water with the containing additives and the solid content were well mixed in a laboratory intensive mixer (RV02, Maschinenfabrik Gustav Eirich GmbH & Co KG, Germany) at 3000 rpm for 10 min in order to obtain an according to the standard DIN EN 1402 self-flowing, yet stable slip. During the mixing the slip was examined several times on visible agglomerates. The slip was characterized as stable if there was no water layer on the slip surface visible after five minutes and self flowing if it was running in one stream from a trowel and showed a spreading of at least 80%.

After the slips were examined on stability, they were immediately filled into a receiver tank and pumped into the vertical positioned mold by pressurized air applying a pressure of 0.1 MPa for 3 min. With the intention of performing experiments with coarse grain suspensions a commercial pressure slip casting machine (DGM80D, Dorst Technologies, Germany) was modified according to Aneziris et al. [18]. The mold had a size of 200 mm × 200 mm × 38 mm with the sprue in the middle of the rectangular mold. The median pore size d_{50} of the mold was 20 μm. Once the mold was filled, the pressure was increased slowly to 0.8 MPa and kept at that pressure for 30 min. After pressure release the shaped bodies were gently demolded by counter-current pressurized air and hand thereby preventing cracking. However, the demolding had to be conducted as fast as possible to avoid disturbance of the body surface. Subsequently, the green bodies were dried at 40 °C and 110 °C for 24 h in each case and later fired with a heating rate of 3 K min^{-1} at 1650 °C for 2 h in an oxidizing atmosphere.

Table 1
Particle sizes of the used ceramic raw materials.

Product name	Raw material	Labeling	d_{10}	d_{50}	d_{90}
Almatis AR 78	$MgAl_2O_4$	1–3 mm	0.8 mm	1.3 mm	2.25 mm
		0.5–1 mm	250 μm	400 μm	800 μm
		0–0.5 mm	54.84 μm	314.2 μm	653.7 μm
		0–0.09 mm	0.944 μm	19.98 μm	98.34 μm
		0–0.045 mm	0.761 μm	12.80 μm	36.23 μm
Martinswerk MR 70	Al_2O_3	–	0.412 μm	0.791 μm	1.668 μm

2.2. Testing

Since it was one aim to study the material properties, the fired bodies had to be cut with a buzz saw in order to obtain testable samples. Special care was taken to keep sufficient distance of the position of the cut out samples from the sprue, because the sprue turned out to be a source of visible cracks.

The modulus of rupture at ambient temperature was determined according to the standard DIN EN 993-6 using three-point bending.

The elastic modulus of cut samples was measured in accordance with the standard DIN EN 843-2. First flat rectangular bars with a size of about 150 mm × 25 mm × 6 mm were cut out of the bodies and then excited with an impulse. The flexural resonance frequency was detected at room temperature with a resonant frequency damping analyzer of IMCE, Belgium. The elastic modulus can be calculated according to the Eq. (2), as mentioned in the standard.

$$E = 0.9465 \frac{m \cdot f_f^2}{w} \frac{l^3}{t^3} \left(1 + 6.585 \left(\frac{t}{l}\right)^2\right) \quad (2)$$

m mass, f_f flexural resonance frequency, w width, l length, t thickness

Additional to the mechanic properties the apparent porosity, the bulk density and pore size distribution of samples cut both from the top as well as from the bottom of the bodies were evaluated, with the intention to reveal gradients caused by segregation and sedimentation. The testing methods were the standards DIN EN 993-1 using the water immersion method and DIN EN 993-3 using mercury porosimetry (Thermo Electron Pascal440, Thermo Fisher Scientific Inc., USA), respectively.

With the aim to investigate gradients caused by sedimentation and segregation as well as cavities the fired bodies were examined by computer tomography (CT-Alpha-225, ProCon X-Ray GmbH, Germany) before cutting. In addition the integration and dispersion of the coarse grain in the ceramic matrix of the cut samples were studied by reflected-light microscopy with a minimum magnification.

2.3. Statistical analysis

From all tested bodies samples were taken from the top and from the bottom with the intention to evaluate gradients in the microstructure and of mechanical properties caused by possible sedimentation and segregation. In addition, the same sample size was chosen for both slip compositions for each test. In order to compare the differences between the top and the bottom of the body as well as between the compositions of different maximum grain size two-tailed Student's t-tests with a level of significance of $p < 0.05$ assuming equal variances were performed using the standard package of the software R [19,20].

3. Results and discussion

As discussed previously, the main purpose of this work was the pressure slip casting of suspensions with coarse grain particles and the assessment of the material properties. With the aid of a modified additive system as presented above it was possible to cast large oxide ceramic bodies.

3.1. Slip preparation and casting

Krieger and Dougherty [21] formulated an equation describing the relationship between the volume fraction of solids in a suspension and the suspension's viscosity. Especially when the volume fraction of solids reaches very high values, the viscosity increases sharply. As in the case of this study, even very small changes of the water content of about ≈0.4 wt.% changed the rheology of the slip remarkably in terms of improved flowability. Therefore, it was crucial to adjust the water content carefully for each slip composition. However, the water content where the change of the rheology from paste-like to flowable occurred had to be kept constant between the casts of the same slip composition. The stated amount of water and additives were therefore found to be the optimum for the tested slips.

The pumping of the slips into the mold with pressurized air only seldom let to plugging of the tube and generally allowed a complete filling of the mold. The plugging might have been caused by segregation attributed to a too low filling pressure causing a slower flowing.

The demolding of the formed bodies by hand and countercurrent pressurized air through the mold only infrequently led to material left on the mold. The demolding of the bodies was only rarely problematic and occurred only when the mold was not filled completely due to plugging of the tube leading to scrap. The demolded and fired bodies showed a smooth surface with very few blow holes and other cavities.

3.2. Testing results

In Fig. 1 the modulus of rupture of cut out bending samples with different maximum grain size are compared. The median of the measured fracture stress for both slip compositions was about 30 MPa. The interquartile range for the slip with a maximum grain size of 1 mm was somewhat larger, but there

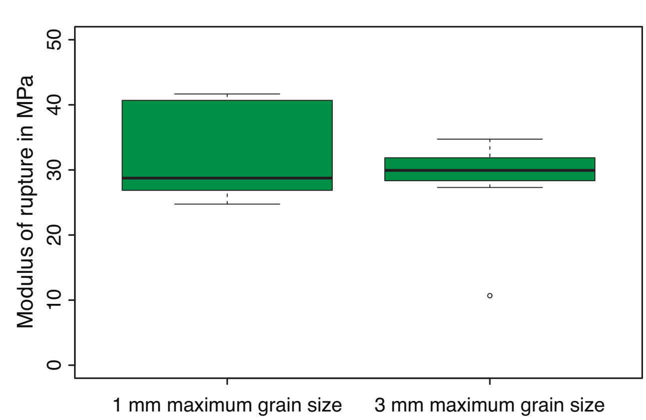

Fig. 1. Modulus of rupture of cut out samples with different maximum grain size at room temperature.

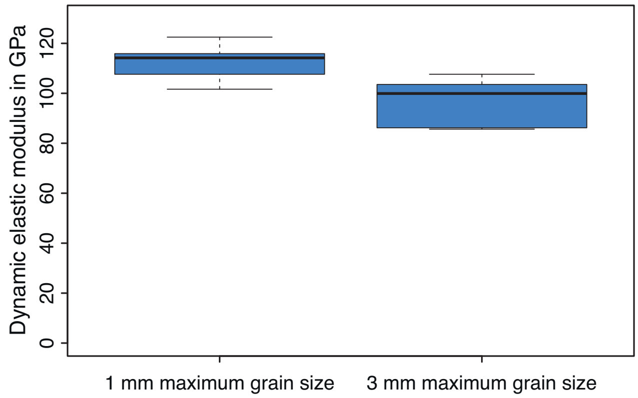

Fig. 2. Dynamic elastic modulus of flat rectangular bars with different maximum grain size.

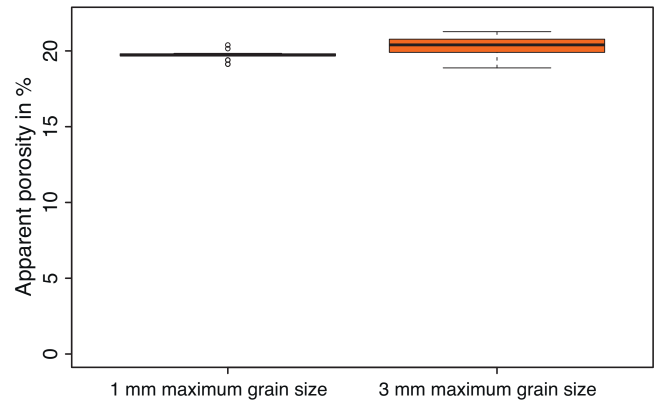

Fig. 4. Apparent porosity of cut out samples.

was no outlier observed as for the slip containing 3 mm grain size. The outlier could be attributed to a cutting too close to the sprue or simple statistical dispersion. The calculated p-value for the two sample Student's t-test of the modulus of rupture was 0.37 with 15 degrees of freedom (16 samples), suggesting no difference in modulus of rupture of samples from both slips.

Similar results were found comparing the modulus of rupture of samples obtained from the top and the bottom of the same body. Therefore, a paired two sample Student's t-test of the differences of the modulus of rupture was performed. The p-value of the t-test was calculated at 0.25 at 7 degrees of freedom (8 comparisons). Consequently, it can be assumed that there is no difference in modulus of rupture between the top and bottom samples.

From Fig. 2 it can be seen that the median of the dynamic elastic modulus of the samples of the slip composition with 3 mm grain size is about 100 MPa and for slips with 1 mm maximum grain size it is slightly higher with 115 MPa. A two sample t-test with 11 degrees of freedom (12 observations) results in a p-value of 0.008. Therefore the results clearly indicate the favorable properties of added coarse grain on lowering the elastic modulus.

As evident in Fig. 3 the pore size and and total open porosity decreases to some extent from top to bottom of a body and with smaller maximum grain size, similar to the results from the apparent porosity measurement.

Fig. 4 plots the data of the apparent porosity for cut out samples for both slip compositions. The sample mean of the apparent porosity of the composition containing a maximum grain size of 1 mm was 19.69% and was only slightly higher for the composition containing 3 mm grain size having an apparent porosity of 20.29%. The p-value for the two sample t-test was 0.003 with 39 degrees of freedom, showing a statistical significant difference of the apparent porosity of the slip compositions.

In data not shown the differences between the apparent porosity of samples taken from the top and the bottom of the same bodies were compared as well. Without exception the samples from the top of the bodies had a lower apparent porosity than the ones from the bottom. The absolute mean difference of the apparent porosity was 0.30% for the 3 mm composition and 0.11% for the 1 mm one. These differences of the apparent porosity relative to the total apparent porosity on the other hand are only 1.5% and 0.6%, respectively and therefore barely measurable. Thus, it can be assumed that the gradients causing a different apparent porosity from top to bottom in the bodies due to sedimentation and segregation are negligible.

This result was confirmed by computer tomography. As shown in Fig. 5, the coarse grain is distributed homogeneously in the whole body and no sedimentation or segregation is

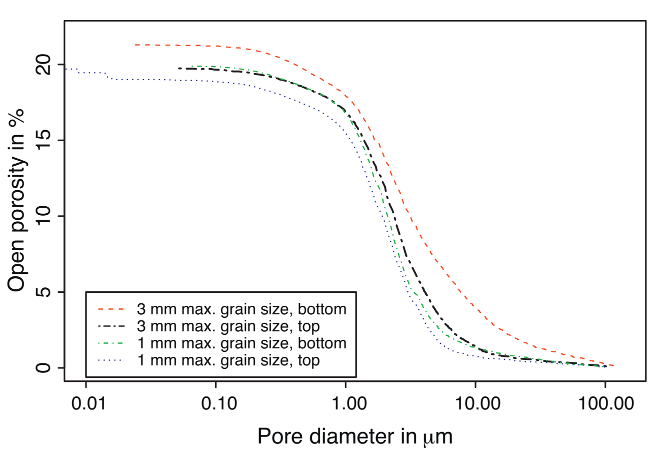

Fig. 3. Open porosity measured with mercury intrusion of samples taken from the top and the bottom of the bodies.

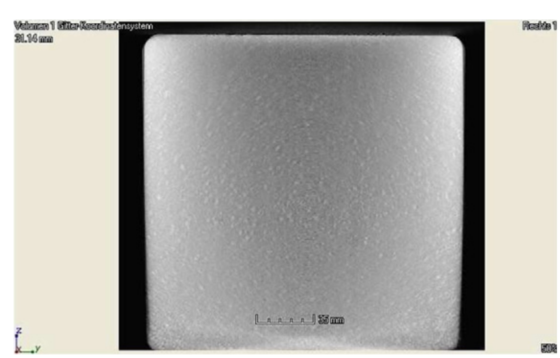

Fig. 5. Cross section of full body with 3 mm grain size.

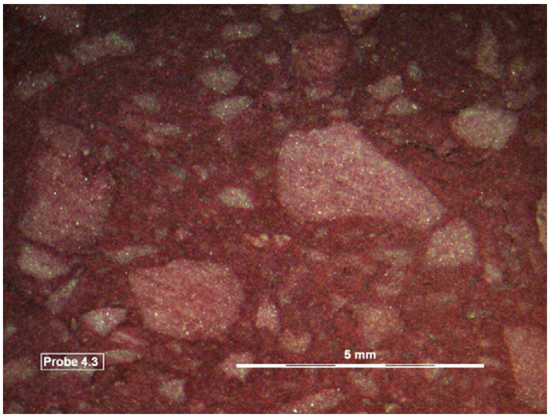

Fig. 6. Cut sections of a fired MA spinel body.

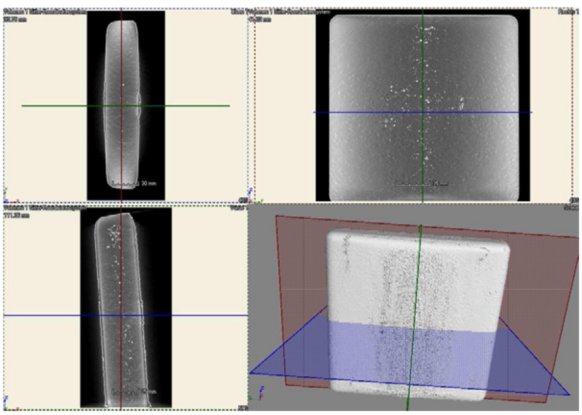

Fig. 7. Pore distribution in a full body with 3 mm grain size.

visible. Similar results were found from reflected light microscopy of cut samples, as shown in Fig. 6. Nevertheless cracks are observed around the coarse grain which could deteriorate the material properties.

Fig. 7 shows that the pores are not even distributed, but concentrated in the center at the vertical axis of the body perpendicular to the filtration direction. This result is in good agreement with previous works and could be avoided by unidirectional casting only [6].

Fig. 8 shows the size and quantity of the pores in a full body with 3 mm grain size. The largest cavity found had a volume of only 12.1 mm^3, though most of the pores had a volume smaller than 1 mm^3.

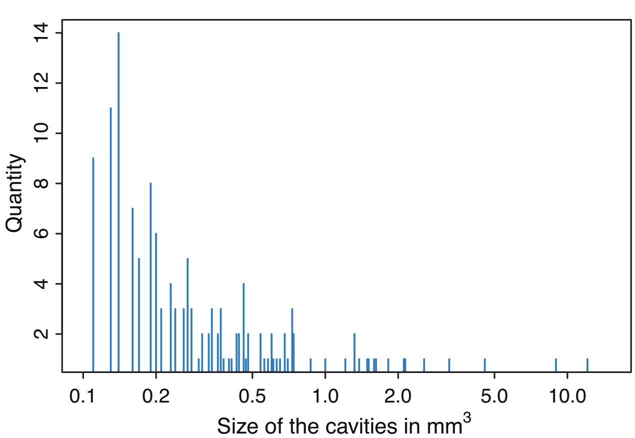

Fig. 8. Pore sizes and pore quantities of a solid body with 3 mm grain size measured with CT.

4. Conclusions

This study investigates the production of large formed alumina rich magnesia aluminate spinel ceramics by pressure slip casting of coarse grain suspensions with particle sizes of up to 3 mm. In addition the achieved material properties are discussed.

It was possible to formulate a stable and pumpable slip as well as perform the demolding of the bodies without cracking, deformations or other damages by adding a minimum of an organic additive system only. Furthermore remarkable good material properties were achieved. Together, these results extend the previous work of Klippel et al. and undeniable show the possibility of expanding the field of application of pressure slip casting. It should be possible to produce large, near-net shape and complicated formed refractories and other parts used for high temperature applications with organic binders only. Future work will further investigate the possibility of casting other oxide ceramic systems and the further improvement of the matrix properties. Furthermore a comparison with other ceramic shaping processes will follow.

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