

## Gelcasting of Zirconia Using Agarose

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**Gelcasting of zirconia with agarose as a gelling agent was evaluated, and the rheological behavior of the suspensions was studied. For certain compositions, a viscosity low enough for the suspensions to be processed as well as a sufficient wet green strength to avoid deformation of cast components due to mechanical stresses was obtained. Furthermore, it was possible to increase the storage modulus of the cast material by a reduction of the gelation temperature, which facilitated demolding. Sintered densities above 99% were achieved and high bending strength was obtained. The results show that the shaping technique has the potential to be used for fabrication of advanced zirconia materials.**

### I. Introduction

As ceramics are introduced in new areas and applications, the requirements of the materials such as performance, reliability, shape, and dimensional tolerances that can be obtained are continuously increasing. This means that several of the conventional forming techniques traditionally used do not meet these requirements.<sup>1</sup> The colloidal processing techniques have the potential to improve the microstructural control of ceramic materials as undesired agglomerates can be removed and ceramic suspensions with a high homogeneity can be obtained.<sup>2,3</sup> To take advantage of these colloidal processing techniques for shaping ceramics, it is further required that the fluid suspension be transformed into a rigid structure while the homogeneity of the suspension is preserved. Gelcasting was developed for this purpose where a gelling agent is added to the suspension of a ceramic powder.<sup>4</sup> The mixture was poured into a non-porous mold where the gelling agent was either chemically or thermally induced to form a rigid gel structure that retained the ceramic particles. Without any external forces during the gel formation, gelcasting has the potential to achieve very homogeneous green bodies without density gradients. This makes the gelcasting technique suitable for fabrication of ceramic materials where strength and reliability are required for fabrication of components with varying thickness or complex shapes.<sup>3</sup>

In the early gelcasting systems developed, acrylate monomers were used as gelling agents in organic solvents.<sup>5</sup> Owing to the toxicity of these systems, various alternative water-based monomer systems have been proposed but some health concerns remain when dealing with the monomers used.<sup>6</sup> In order to avoid the hazardous problems with monomers, other gelcasting systems have been evaluated. Proteins<sup>7</sup> and naturally occurring polysaccharides such as agar and agarose<sup>8</sup> have been used as gelling agents. Unlike most gelcasting systems, which form a gel as the temperature is increased, the agar system forms a gel on cooling and thus shows large similarities to the principles of injection molding. A major exception is that an additional stage

for binder burnout is not needed as the amount of agar used for consolidation is only around 1 wt% based on the water.

For evaluation of alternative gelcasting systems containing agar products, alumina is the most common ceramic materials used.<sup>8–11</sup> Examples of other materials that have also been studied for these systems are silicon nitride<sup>12</sup> and porcelain,<sup>13,14</sup> while the use of zirconia has not been reported. Even when other gelcasting systems are considered, the use of zirconia was found to be rare and this might be related to the difficulties reported into processing zirconia suspensions.<sup>15</sup> To take advantage of the transformation toughening of zirconia also in gelcasting, most of the efforts have been directed toward zirconia-reinforced alumina<sup>15,16</sup> materials using monomer-based systems. It has, however, been shown that gelcast zirconia materials can reach high sintered densities even with low solids loadings when a fine powder is used.<sup>17</sup>

When agar was introduced as a gelling agent for casting of ceramic suspensions by Fanelli *et al.*,<sup>8</sup> the work covered the entire ceramic fabrication process from preparation of suspensions to mechanical evaluation of densified materials. The solids loadings used for this work were below 40 vol%, and, for alumina-sintered densities, around 94% was reached. In order to further improve the sintered density, an increased green density was thus required, which, for gelcasting, is closely related to the solids loadings of the suspension used. Most of the work performed with these agar-based systems has since then been related to formulation and rheological evaluation of suspensions. Through this process development, solids loadings have been increased to 50–60 vol%, and sintered densities around 98–99% have been obtained.<sup>9,11</sup> However, very little has been done to evaluate the performance of cast and sintered materials obtained from these agar-based gelcasting systems.

The aim of this work was to investigate whether the gelcasting system with zirconia and agarose can meet the requirements for fabrication of materials with high performance and complex shapes. The rheological behavior of ceramic suspensions, shrinkage, and deformation during drying as well sintered materials have been evaluated.

### II. Experimental Procedure

The zirconia powder (TZ-3YS-E, Tosoh, Japan) used for preparation of ceramic suspensions with a solids loading of 50 vol% was planetary ball milled (PM 400, Retsch, Germany) with 0.3 wt% of dispersant (Dolapix PC75, Zschimmer & Schwarz, Germany). Agarose (D1 LE, Hispanagar, Spain) was selected as a gelling agent after evaluation of several polysaccharide products. Solutions with a concentration of 2 wt% of agarose were prepared in a water bath at 90°–95°C for 2 h in order to avoid occurrence of undissolved agarose in the ceramic suspension. The zirconia suspension was stirred and heated to 60°–65°C in a closed vessel using a water bath before water and agarose solution, both tempered to 70°C, were added in quantities needed to achieve different compositions between 20 and 39 vol% of zirconia and an agarose content between 0.25 and 1.0 wt% based on water (which corresponds to around 0.1–0.4 wt% based on zirconia for a solids loading of 30 vol%). The pH of the suspension used for gelcasting was around 8.1 at 65°C. Continued mixing and evacuation at an underpressure of 75 kPa were also performed in a closed vessel at 60°–65°C for 45 and 15 min, respectively.

G. Messing—contributing editor

Manuscript No. 21332. Received January 6, 2006; approved February 27, 2006. Presented at the 9th International Ceramic Processing Science Symposium, Coral Springs, FL, Jan. 8–11, 2006.

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### (1) Rheology

The rheological behavior was conducted with a rheometer (StressTech Rheometer, ReoLogica Instruments, Sweden). The sample container was covered with a plate to prevent evaporation and thermal leakage. A preshear of  $400 \text{ s}^{-1}$  for 1 min and a pause for 30 s were performed before the viscosities were measured at shear rates of 1, 5, 20, 80, 200, 400, and  $700 \text{ s}^{-1}$  at  $60^\circ\text{C}$  for both pure polysaccharide solutions and for zirconia suspensions. The viscosity of the pure zirconia suspension was also studied as the temperature was increased from  $25^\circ$  to  $95^\circ\text{C}$  at a shear rate of  $200 \text{ s}^{-1}$ . The gelling behavior was studied for both pure polysaccharide solutions and for zirconia suspensions by measuring the storage modulus for an oscillation of 1 Hz during cooling at a rate of  $1^\circ\text{C}/\text{min}$  from  $60^\circ$  to  $25^\circ\text{C}$  or  $5^\circ\text{C}$ .

### (2) Shrinkage, Densification, and Deformation

Cylindrical samples were cast in molds with a diameter of 25 mm. The samples were sintered at temperatures between  $900^\circ$  and  $1500^\circ\text{C}$  for 2 h at a ramp rate of  $5^\circ\text{C}/\text{min}$  in an air atmosphere. The drying shrinkage was determined from the diameter of the cylindrical samples measured with a slide caliper, and the densities were measured by water intrusion. Spheres cast in machined molds with a diameter of 20 mm were used to evaluate deformation due to mechanical stresses. The spheres had one small flat surface with a diameter of 4.4 mm upon which the spheres were placed after demolding. The surfaces of the spheres were digitized by a three-dimensional scanner (ProCera Piccolo, Nobel Biocare, Sweden) when sintered at  $900^\circ$  and  $1500^\circ\text{C}$ . The shrinkage and deformation of the cast spheres were determined when compared with the CAD model using a three-dimensional CAD program. Bars with a size of  $75 \text{ mm} \times 8 \text{ mm} \times 8 \text{ mm}$  were cast from suspensions with a solids loading of 30 vol% and an agarose content of 0.75 wt% for evaluation of warpage due to symmetrical and unsymmetrical drying.

### (3) Mechanical Behavior

The mechanical performance of the cast materials was evaluated from plates cast from suspensions with a solids loading of 30 vol% and an agarose content of 0.75 wt%. The plates were presintered at  $900^\circ\text{C}$  and cut into bars before sintered at  $1500^\circ\text{C}$ . As a reference material for the mechanical evaluation, bending bars were cold isostatically pressed at 200 MPa using a pressing powder (TZ-3YB, Tosoh). The same sintering procedure was used for both materials, except for an additional burnout stage introduced for the pressed materials. The surfaces of the bending bars were machined to  $3 \text{ mm} \times 4 \text{ mm}$  and chamfered. The bars were evaluated by four-point bending with 40 mm between the outer rollers and 20 mm between the load points using a materials-testing machine (Z050/SN3A, Zwick, Germany). The fracture surfaces of the bend tested bars and polished surfaces of cast materials were studied with a scanning electron microscope (JSM-5300, Jeol, Japan).

## III. Results and Discussion

Agar can be dissolved in boiling water and when cooled below the glass-transition temperature, hydrogen bonds are established, which form double helix structures and a gel network. To avoid an incomplete dissolution of the agar and an exposure of the ceramic suspensions to temperatures where the suspension may no longer be stable, the agar solution is prepared separately. Thus, the ceramic suspension must be heated before the agar solution can be added and kept at a temperature well above the glass transition temperature during the remaining processing in order to avoid gel formation. The amount of agar additions required to obtain a gel is very low and the binder burnout stage used for other gelcasting systems is thus of less importance.<sup>18</sup>

Several agar products were evaluated in water and ceramic suspensions. The results showed large variations in both viscosity and storage modulus. The most favorable results were obtained

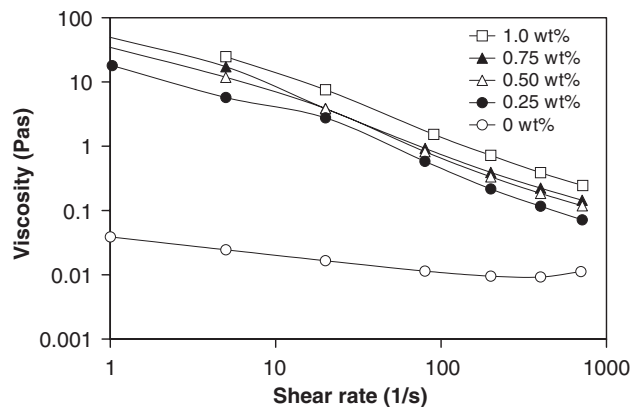


Fig. 1. The viscosity of zirconia suspensions at  $60^\circ\text{C}$  with a solids loading of 33 vol% and varied agarose contents.

for agarose, which is a purified agar consisting of repeating units of alternating  $\beta$ -D-galactopyranosil and 3,6-anhydro- $\alpha$ -L-galactopyranosil groups. Thus, the amount of impurities from the agarose used was even below the level of impurities already present in many technical ceramics. Agarose was then chosen for the study to evaluate the use of polysaccharides for gelcasting of zirconia.

### (1) Viscosity of the Suspension

The viscosity of the pure zirconia suspension was studied at increasing temperature to evaluate the stability of the ceramic suspension at the temperatures needed to avoid gel formation when the agarose solution was added. The viscosity was found to decrease slightly from  $25^\circ$  to  $90^\circ\text{C}$ , where it increased due to instability of the suspension at temperatures above  $90^\circ\text{C}$ .

When agarose was added to the zirconia suspensions, even small amounts of agarose around 0.25 wt% caused the viscosity of the suspension to increase significantly, from below 0.1 to around  $10 \text{ Pa}\cdot\text{s}$  at low shear rates. As the amount of agarose was further increased up to 1.0 wt%, the viscosity continued to increase continuously to around  $60 \text{ Pa}\cdot\text{s}$  at low shear rates (Fig. 1). A more continuous change in viscosity was obtained as the solids loading was varied between 20 and 35 vol% (Fig. 2).

### (2) Consolidation

In contrast to most of the conventional gelcasting systems where a temperature increase is used to initiate the gel formation, the agarose system forms a gel on cooling. As the temperature of an agarose solution was reduced, gel formation was initiated around  $33$ – $25^\circ\text{C}$ , depending on the agarose concentration, while gelation in the ceramic suspensions was initiated in a more narrow temperature range of around  $32^\circ\text{C}$ .

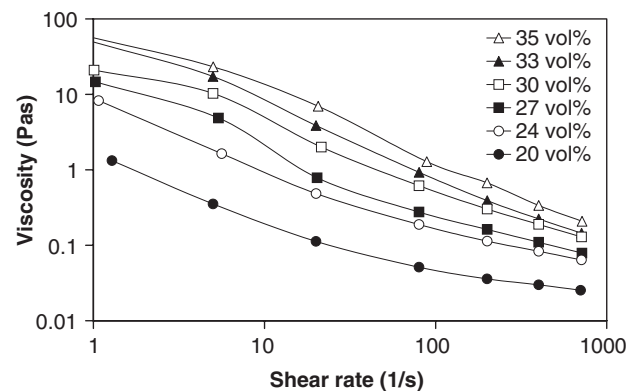


Fig. 2. The viscosity of zirconia suspensions at  $60^\circ\text{C}$  with varied solids loadings and an agarose content of 0.75 wt%.

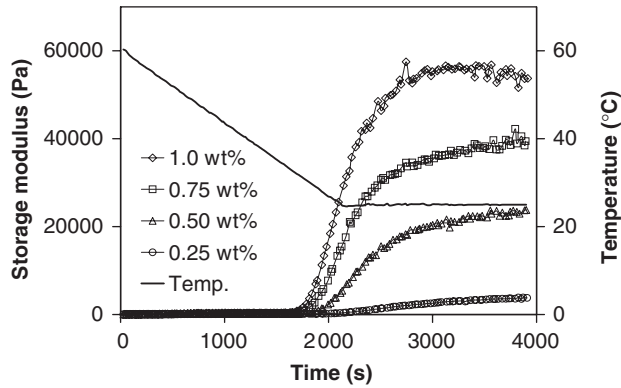


Fig. 3. The storage modulus for suspensions with a solids loading of 33 vol% and varied agarose contents.

When studying the gelling behavior of pure agarose solutions and of suspensions, it could be concluded that the storage modulus increases with an increased agarose content (Fig. 3), due to the occurrence of more potential hydrogen bonding sites and shorter distances between these sites, which creates a more rigid network. As the solids loading of the suspension was increased, with a fixed amount of additives, an increased storage modulus would be expected due to an increased rigidity of the cast material as the ceramic particles come in closer contact with each other (Fig. 4). However, in the agarose system studied, the storage modulus increased continuously to around 43 kPa at a solids loading of 27 vol%, followed by a decrease to around 26 kPa at a solids loading of 30 vol%. A similar change in storage modulus also occurred for other agarose concentrations. This might be because the formation of a well-structured network of the agarose gel is disturbed as the distance between the ceramic particles is reduced. As the solids loading is further increased, the storage modulus increases again, which may be caused by segregation where areas with higher agarose concentrations are formed.

### (3) Methods to Further Increase Rigidity of the Formed Gel

The stiffness of the gel formed from these systems where agar or agarose are used have been shown to be sufficient for shaping parts with complex shapes<sup>9,13</sup> but the strength of the cast materials is still rather low. It is thus important to further increase the rigidity and strength of the cast materials in order to avoid deformations due to mechanical-related stresses during demolding, handling, and drying. When it is not possible to improve the rigidity by increased solids loading or agarose content due to restrictions of the viscosity of the suspension, other methods have been evaluated. Therefore, some attempts have been made to utilize a synergistic behavior to increase the strength of the gel by combining agar with other polysaccharides.<sup>19</sup> Another pos-

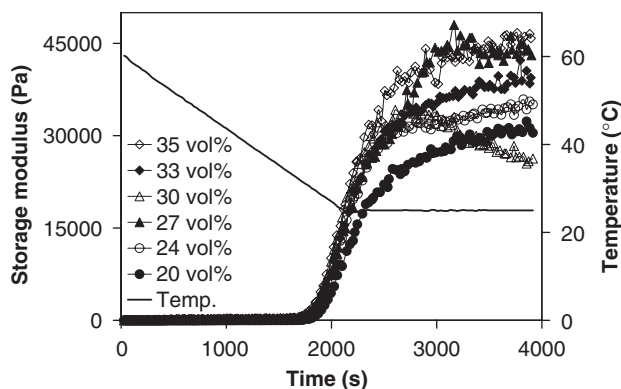


Fig. 4. The storage modulus for suspensions with varied solids loadings and an agarose content of 0.75 wt%.

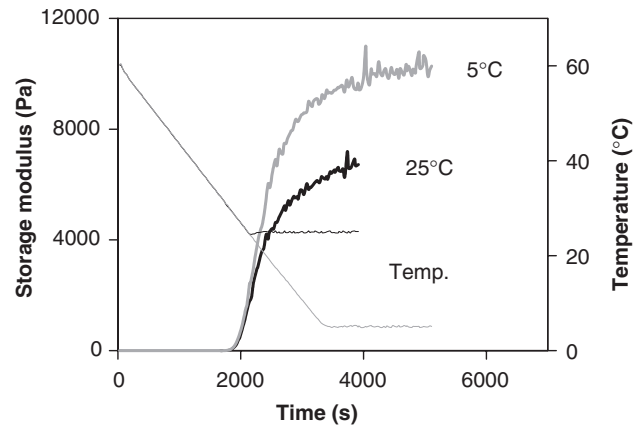


Fig. 5. The storage modulus for solutions with 0.75 wt% agarose cooled to 5° and 25°C.

sibility to obtain an increased rigidity of the gel is by reducing the temperature after casting. When the end temperature was reduced from 25° to 5°C, the storage modulus was found to increase by around 40% in both the pure agarose gel (Fig. 5) and the consolidated zirconia suspension (Fig. 6). This increase in the storage modulus when the suspension was cooled to a lower temperature was likely to be due to the formation of a more ordered gel structure.<sup>20</sup> Furthermore, the improved rigidity of the gel facilitates demolding and handling of cast parts as the risk for deformation would be reduced.

### (4) Drying Shrinkage, Green Density, and Densification

The relatively low solids loadings of the suspensions resulted in a large drying shrinkage. As the solids loading decreased from 39 to 24 vol%, the linear shrinkage increased from 6% to 23% (Fig. 7) and the green density decreased from 52% to 46%. However, no significant influence of the agarose content on shrinkage or green density was found. With the assumption that homogeneous green bodies were obtained, an increased green density would not only reduce the remaining pore volume, the average pore size would also be reduced and would result in an improved sintering performance. A predefined density can then be reached at a lower sintering temperature as shown in Fig. 8, while no variations in green densities or sintering performance were found when the agarose content was varied (Fig. 9). When the cast materials were sintered at 1500°C, independent of solids loading or agarose content, the temperature was sufficient for all materials to reach sintered densities above 99% (Figs. 8, 9). These results show that a high solids loading is not always required as often claimed for direct consolidation methods in order to reach high sintered densities.<sup>5</sup> The final sintered densities

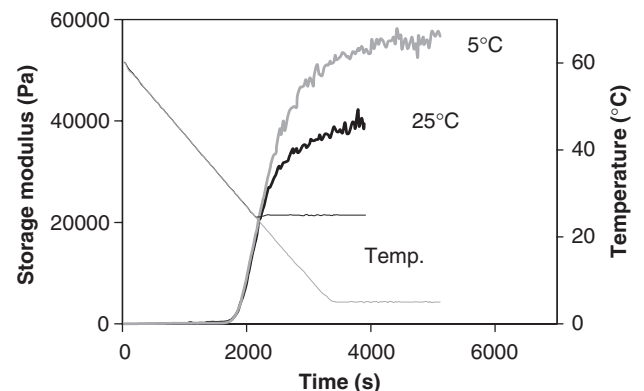


Fig. 6. The storage modulus for zirconia suspensions with a solids loading of 33 vol% and an agarose content of 0.75 wt% cooled to 5° and 25°C.

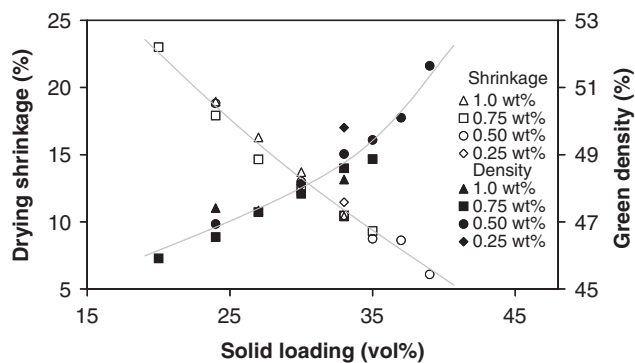


Fig. 7. The linear drying shrinkage and green density of materials cast from suspensions with varied solids loadings and agarose contents.

that can be reached are also closely related to the homogeneity obtained in the green body.

### (5) Deformation of Cast Materials

The advantage of the gelcasting systems is the possibility of obtaining materials with an extremely high homogeneity. In addition to an improved sintering performance, it would further allow a high-dimensional control of cast parts by compensation for the shrinkage during drying and sintering. However, deformation can arise even in a cast material with a high homogeneity. These deformations may be caused by non-uniform drying or mechanical influence and become especially important to consider for gelcasting systems that have a larger drying shrinkage or weak wet green bodies. The agarose system is such a system where the cast materials have a relatively low wet green strength and therefore it is important to ensure that the cast parts are not exposed to stresses that can cause deformation during demolding and handling. Deformation during drying or warpage is caused by stresses due to nonsymmetrical shrinkage.<sup>21</sup> This may not only result in a nonhomogeneous green density, but would further reduce the dimensional tolerances that can be reached. These problems are usually tackled by increasing solids loading to reduce the drying shrinkage or by using more gentle drying conditions with a higher humidity in order to reduce the stress gradients. The warpage may be reduced somewhat with these actions; however, a more uniform drying process is required in order to further reduce or even avoid warpage.

To evaluate the deformation of the cast materials caused by insufficient wet green strength, cast spheres were used (Fig. 10). Owing to the symmetrical shape used, drying-related deformations could be avoided. Any deformation detected on the cast sphere when compared with the ideal model would then be related to the mechanical stresses from the weight of the sphere

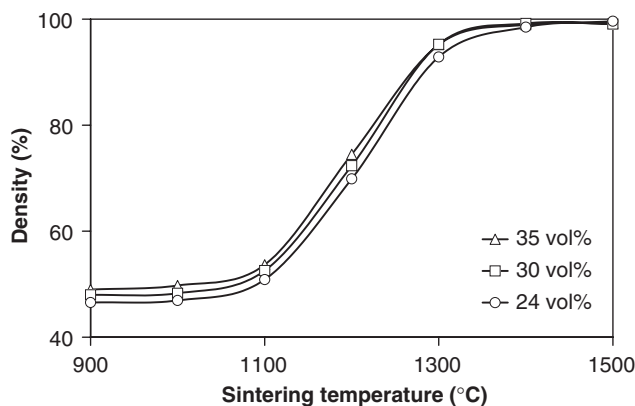


Fig. 8. The density for materials cast from zirconia suspensions with varied solids loading and an agarose content of 0.75 wt%.

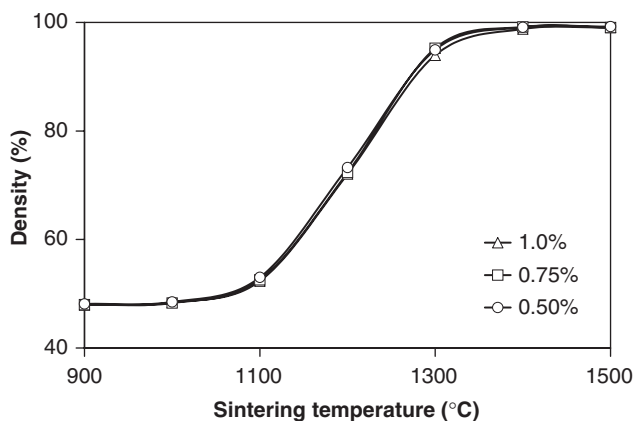


Fig. 9. The density for materials cast from zirconia suspensions with a solids loading of 33 vol% and varied agarose contents.

due to insufficient rigidity in the wet green body. To maintain the orientation of the sphere during drying, one side of the sphere had a small flat surface on which they stood during drying. When the shape of the upper part of the spheres was measured with a mechanical scanner, no deformations were found, even for solids loadings down to 20 vol%. This lack of deformation could probably be due to the fact that the upper part of the sphere only was exposed to minor stresses. The small flat surface at the lower part of the sphere was exposed to the weight of the sphere, which corresponded to a pressure of around 5–7 kPa, depending on the composition of the suspensions used. With a solids loading and an agarose content of 33 vol% and 0.75 wt%, respectively, the strength was sufficiently high for the cast sphere to retain its shape during drying. As the solids loading or the agarose content was reduced, the strength was also reduced and deformation was detected.

The relatively large drying shrinkage of the cast materials using the agarose system turned out to be beneficial for the evaluation of drying-related deformations as the warpage was then amplified. Instead of reducing the warpage by changing the total shrinkage using an increased solids loading, the influence of the uniformity of the drying process was evaluated. The cast bars used were then dried under symmetrical and unsymmetrical conditions. Symmetrical drying was obtained by only allowing the bars to dry from two opposite surfaces. The stress gradients formed during the drying would then be of equal magnitude and of opposite direction and thereby not cause any deformation (Fig. 11). The unsymmetrical dried bars were allowed to dry from both two opposite sides and the upper surface. The compressive stresses formed at the upper surface caused the bar to

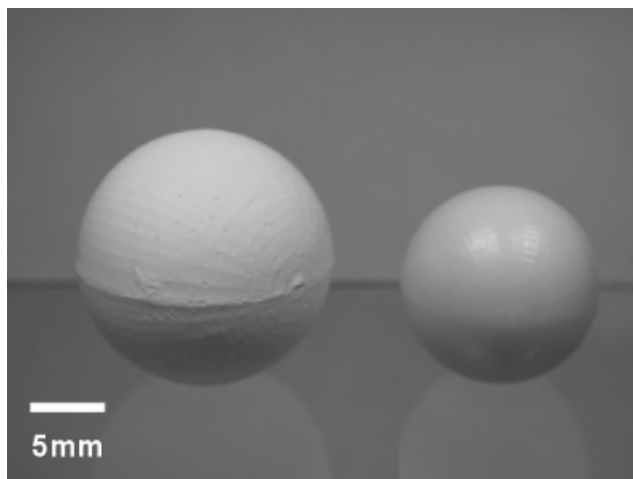


Fig. 10. Cast spheres (green and sintered) used for evaluation of deformation.

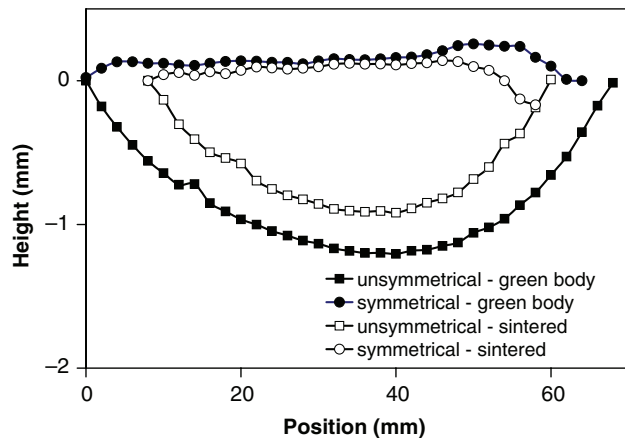


Fig. 11. The change in height along cast bars dried during symmetrical and unsymmetrical conditions before and after densification.

bend significantly, as there were no opposite stresses present at the lower surface. The results showed the importance of symmetrical drying and how the shape of the cast material can be maintained even without extreme solids loadings or gentle drying conditions. The small warpage at the ends of the uniformly dried bars was due to the boundary conditions where it was difficult to control and avoid non-uniform drying. The shape of the bars after densification was very close to the shape of the green bodies and showed that the deformation caused during drying also remained after sintering. These results further indicate that it would be favorable to consider the drying process even in the design stage of the ceramic parts to be cast in order to improve the dimensional tolerances that can be reached.

#### (6) Microstructure and Mechanical Properties

The microstructure of the sintered material showed a grain size below  $1\ \mu\text{m}$  and small pores with a diameter of approximately  $1\ \mu\text{m}$  evenly distributed in the material (Fig. 12). These small pores were found with equal frequency in all materials independent of the solids loading used and were thus not related to an increased difficulty to remove air from the suspension as the viscosity was increased. These small pores may instead be related to the fact that the evacuation cannot be performed at the same low pressure as usually used for evacuation of suspensions at room temperature as this would cause the heated suspension to boil. The slightly more gentle evacuation procedure used may thus not have been sufficient to remove the smallest air bubbles from the suspension.

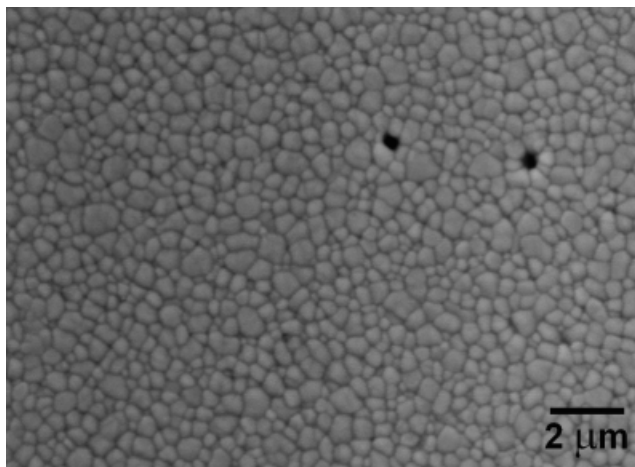


Fig. 12. Microstructure of materials cast from suspensions with a solids loadings of 30 vol% and an agarose content of 0.75 wt% sintered at  $1500^\circ\text{C}$ .

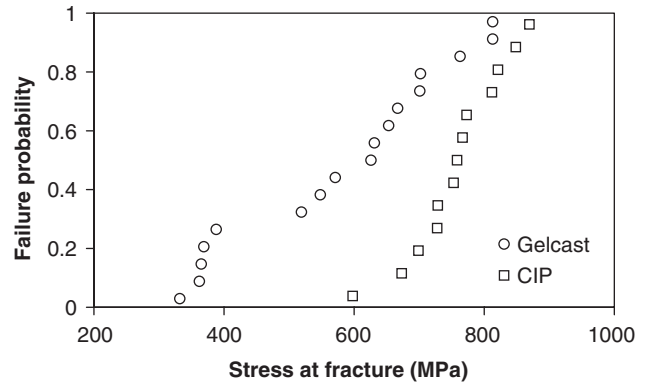


Fig. 13. Failure probabilities of gelcast and cold isostatically pressed (CIP) materials calculated with Weibull statistics.

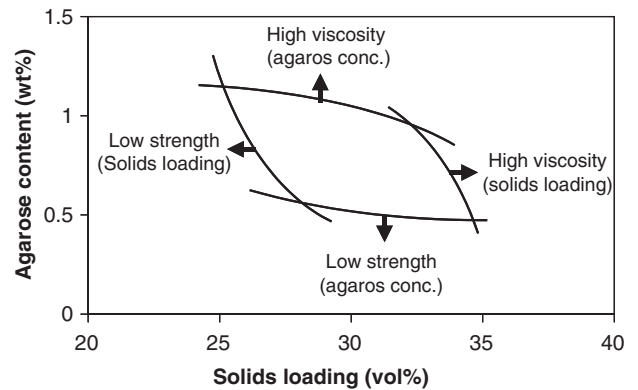


Fig. 14. Composition of the ceramic suspensions that were found suitable for casting.

The failure probabilities calculated with Weibull statistics indicated that two major flaw populations were present in the cast materials (Fig. 13). In the range between 300 and 400 MPa, the fracture origin was related to the occurrence of larger pores, with a size around  $100\ \mu\text{m}$  that was either not successfully removed from the suspension during evacuation or introduced during handling of the suspension at the casting procedure. The remaining bars fractured between 500 and 800 MPa, where the major flaws originated from agglomerates. These results can be compared with cold isostatically pressed materials that reached a strength between 600 and 850 MPa where the major flaws were related to intergranular cavities.

#### (7) Practical Use of the Agarose Gelcasting System

The compositions of the ceramic suspensions that were found suitable for casting are determined by the viscosity of the suspension and the strength of the cast green body (Fig. 14). When the solids loading or the agarose content was too high, the viscosity reached a level where it became difficult to fill the molds. When the solids loading or the agarose content was reduced too much, the strength of the wet green bodies reached a level where deformation occurred due to stresses from the weight of the cast part. Within these limitations, compositions were found that were suitable to use for casting of the spherically shaped parts (Fig. 10). As the desired shape of the cast green body is changed, the stresses will also change and result in an expansion or compression of the compositions that is suitable for use.

## IV. Conclusions

Gelcasting with agarose as a gelling agent was evaluated for casting of zirconia. The compositions of the ceramic suspensions

that were found suitable for casting, were determined by the viscosity and the strength of the cast green body. With a suitable composition of the suspension, the shape of the cast components could be maintained and sintered densities above 99% were reached, even though the solids loading was lower than usually claimed to be required. The mechanical evaluation of the cast and sintered materials showed that strength values similar to cold isostatically pressed materials can be reached with the agarose system. The prepared suspensions were also used to cast various shaped components and the demolding was facilitated by an improved rigidity of the wet green body achieved by a further decrease in the temperature during consolidation. The warpage during drying was shown to be strongly related to the uniformity of the drying process. This further indicates that deformations of cast materials can be avoided even when ceramic suspensions with low solids loadings are used.

### Acknowledgments

The author thanks T. Oddstig for skillful experimental assistance, M. Andersson at Nobel Biocare AB for the use of equipment for scanning and evaluation of the shape of cast materials, and the company Hispanagar, Spain, for their kind supply of agarose for the work.

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