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Osmotic drying of gelcast bodies in liquid desiccant

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Abstract

Osmotic drying of gelcast alumina bodies was carried out in water solutions of various polyethylene glycols (PEGs) with molecular weight ranging from 1000 to 80,000 g/mol. Up to 30% of the water content could be removed from the gelcast bodies immersed in a 43 wt% solution of PEG 80000. It was found that PEG 1000 was a less effective desiccant than the PEGs with higher molecular weights, even if the osmotic pressure was similar (4.9 MPa). The smaller PEG molecules penetrated the gelled bodies and reduced the dewatering. Moreover, the penetrated PEG molecules affected the pore structure of green bodies and in this way influenced the sintering behaviour. The time dependence of dewatering and the effect of the size of gelcast bodies were investigated and correlated with the green body structure and sintering behaviour in order to optimize the osmotic drying process.

Keywords: Al_2O_3; PEG; Gelcasting; Drying; Osmotic

1. Introduction

Gelcasting is an attractive ceramic forming process for making high-quality, complex-shaped ceramic parts.[1,2] The water-based ceramic suspension with dissolved organic monomers is poured into a mould, polymerized in situ to immobilize the ceramic particles and solvent in a network of organic gel. The gelled ceramic body is removed from the mould while still wet, and then dried and fired. During the preparation of ceramic suspension, it is of advantage to utilize colloidal processing, which is of exceptional importance for reliable and defect-free processing of submicrometre- and nanometre-sized powders with their strong tendency to agglomeration.[3,4] Moreover, gelcasting separates the shaping stage (i.e. the casting stage) of the suspension from the consolidation stage.[1] During the consolidation stage no movement of particles occurs, so the uniform particle dispersion of a stable suspension can be retained in the gelled ceramic body, which finally results in a highly regular particle packing in the green body. However, the inherently lower loading of suspensions prepared with nanopowders[5] results in gelcast bodies that undergo severe shrinkage during drying and are susceptible to warpage and cracking, especially in the case of large cross-sections.[6] The lower the powder concentration of the suspension, the more difficult drying can be expected due to the higher content of organic gel in the gelled ceramic body. The drying of gelled ceramic bodies is controlled by the gel structure.[6,7] The small pores in the gel significantly slow down the transport of water from the body interior to the surface, where it can evaporate. The low water permeability of the gel together with the thick wall of the ceramic body can cause preferential water removal from the surface layer. The developing capillary forces generate tension in the liquid that results in inhomogeneous shrinkage. Often, the drying front can even enter the body, leaving behind a stiff porous surface layer while the centre of the body has an excess of water, i.e. it is still capable of shrinking.[8] Furthermore, the large capillary forces due to small pores in the gel and an irregular drying front can produce flaws in the gel. These flaws can increase under the action of macroscopic stresses and damage the ceramic body.[6]

Osmotic drying of gelcast bodies in a liquid desiccant offers the possibility of removing high local stresses responsible for the formation of such defects.[9,10] Osmotic drying totally prevents capillary stresses from coming into action. During osmotic drying, the body is immersed in an appropriate polymer solution and the gel in the ceramic body acts as a semipermeable membrane. Due to the different chemical potentials of water in the gelcast body and in the surrounding solution, the water is removed from the body. The buoyant support of the gelled body during the drying is another useful feature of osmotic drying, especially in the case of large bodies with different wall thicknesses. Osmotic

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pressure of polymer solution controls the water removal from gelcast bodies and, contrary to air drying, acts uniformly over the whole, even complex-shaped body. Osmotic pressure can be predicted and easily controlled.[11] Osmotic pressure, Π, of an ideal (i.e. very diluted) solution is given by van't Hoff's law:

$$\Pi = RTC \tag{1}$$

where R is the gas constant, T is the absolute temperature, and C is the molar concentration of the solute. Unfortunately, polymer solutions do not obey van't Hoff's law and deviate from this linear function in two ways. Osmotic pressure of a polymer solution is a nonlinear function of concentration and depends on molecular weight. For a non-ideal solution, osmotic pressure can be calculated as:

$$\Pi = RTCM\left(\frac{1}{M} + \alpha CM + \beta (CM)^2 + \cdots\right) \tag{2}$$

where M is the molecular weight of the solute, and α and β are the second and third virial coefficients. These coefficients are empirically determined constants for a given solute–solvent system, and also depend on temperature. The first term in this power series describes the ideal solution. For the calculation of osmotic pressure of polymer solutions the higher (than the second and third) terms in the series are considered negligible. Polyethylene glycol (PEG) is a water-soluble polymer readily available in different molecular weights, which exhibits one of the highest osmotic potentials available.[12] PEG aqueous solutions thus seem to be the most convenient liquid desiccant for osmotic drying of gelcast bodies. The virial coefficients of PEG in aqueous solution were experimentally determined and are given by the equations[12]:

$$\alpha = 2.49\left(\frac{1}{T} - \frac{1}{T_\theta}\right) \tag{3}$$

$$\beta = 29.3\left(\frac{1}{T} - \frac{1}{T_\theta}\right) \tag{4}$$

where the reference temperature $T_\theta = 375.7$ K. The units of the virial coefficients α and β are mol cm^3 g^{-2} and mol cm^6 g^{-3}, respectively. The coefficients are independent of the molecular weight of PEG within the range 200–40,000 g/mol.[13] Recently, this model has been verified to be valid for a molecular mass as high as 500,000 g/mol.[11]

Osmotic drying of gelcast bodies in a liquid desiccant was reported by several authors,[9,10,14,15] who proved the beneficial effect of this drying method. However, they did not examine the effect of the molecular weight of the dissolved polymer. It follows from the above-mentioned analysis that the molecular weight of a dissolved polymer substantially influences osmotic pressure. Another aspect of molecular weight is the size of macromolecules. Osmotic effect can be fully employed only if the polymer does not enter the gel pores.

The objective of the present investigation was to determine the effect of molecular weight of the dissolved polymer in the liquid desiccant on water removal from gelcast bodies. This work also investigates the homogeneity of gelcast bodies after gel burnout and sintering, and tries to correlate it with the drying conditions.

Table 1
Concentration of polyethylene glycols in water solution with osmotic pressure of 4.9 MPa.

Grade	Molecular weight, M_n	Concentration		Supplier
	g/mol	mmol/l	wt%	
PEG 1000	1000	400.91	38.3	Sigma–Aldrich Chemie, Germany
PEG 20000	20,000	21.63	40.2	Sigma–Aldrich Chemie, Germany
PEG 35000	35,000	12.38	40.3	Sigma–Aldrich Chemie, Germany
PEO L-8	80,000	5.42	43.0	Alroko, Germany

2. Experimental

2.1. Preparation of gelcast bodies

Alumina powder (Taimicron TM-DAR, Taimei Chemicals Co., Japan) with a mean particle size of 160 nm and specific surface area of 14.5 m^2 g^{-1} was used for the preparation of gelcast bodies. The alumina powder was dispersed in 15 wt% water solution of organic monomers to obtain a suspension with 47.5 vol% of ceramic powder. Commercial dispersant (0.9 wt% of ceramic powder) Dolapix CE 64 (Zschimmer&Schwartz, Germany) was used to stabilize ceramic particles in the suspension. The ratio of linear monomer to cross-linking monomer was 4:1. Methacrylamide (64090, Fluka, Japan) and N,N′-methylene bisacrylamide (14607, Sigma–Aldrich Chemie, Germany) were used as linear monomer and cross-linker, respectively. Ammonium persulfate (215589, Sigma–Aldrich Chemie, Germany) and tetramethyl ethylene diamine (T22500, Sigma–Aldrich Chemie, Germany) were chosen as initiator and catalyst, respectively. After addition of the initiator and catalyst (1.08 μl of 10% solution per 1 g of the suspension for both initiator and catalyst) the suspension was polymerized in situ in plastic moulds at room temperature under nitrogen atmosphere for 2.5 h. After polymerization, the gelled bodies in the shape of discs (dia. 40 mm – thickness 10 mm, dia. 30 mm – thickness 7 mm) were removed from moulds and carefully washed with water to remove any non-reacted layer.

2.2. Osmotic drying

Polyethylene glycols (PEGs) with different molecular weights were dissolved in deionised water to prepare liquid desiccants. The grades of PEGs and concentration of their solutions are shown in Table 1. Note that high molecular weight grades of polyethylene glycol are often referred to as polyethylene oxides (PEOs). The concentration of the solutions was calculated according to Eq. (2) to obtain a solution of the same osmotic pressure (4.9 MPa) regardless of molecular weight. The graph in Fig. 1 shows the dependence of osmotic pressure on molar concentration for PEGs with different molecular weights. The required concentration for different PEGs is indicated. The value of 4.9 MPa was chosen as the osmotic pressure of the highest

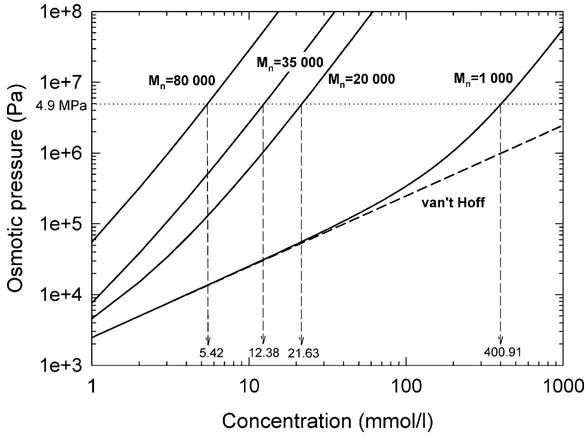

Fig. 1. Osmotic pressure of PEGs with different molecular weights as a function of concentration at room temperature (298 K). The bold dashed line represents the dependence for an ideal solution given by van't Hoff's law. The concentrations corresponding to required osmotic pressure of 4.9 MPa are indicated.

concentration of PEG 80000 still applicable for osmotic drying. The high molecular weight polymers increase the viscosity of a water solution and limit the usable concentration.

Gelled bodies were immersed in water solutions of different PEGs. After preset times the ceramic discs were taken out of the liquid desiccant and carefully washed to remove all PEG solution. The water was then wiped from the body surface with a cloth. The ceramic bodies were weighted before and after osmotic drying. After osmotic drying, the ceramic discs were left at room temperature to fully dry out in air atmosphere for another 3 days, followed by drying at 130 °C for 6 h and weighted again. For comparison, one gelled ceramic disc was dried out in air atmosphere without being exposed to the liquid desiccant. Selected experiments were multiplied to assess the variability in the measurements. Error bars (standard error of the mean) shown in the graphs demonstrate the experimental accuracy.

2.3. *High temperature treatment and homogeneity evaluation*

The organic gel was burnt out from the ceramic bodies by heating to 800 °C. The ceramic green bodies were then sintered at 1300 °C for 2 h in air atmosphere. The density of green bodies after gel burnout and of sintered bodies was determined in water by the Archimedes method. The homogeneity of green and sintered bodies was determined by comparing the densities and pore size distributions of the centre part of the disc with the edge part of the disc. The centre and edge parts were cut off from the original gelcast disc. The shape of the centre and edge parts and their position in the original disc are shown in Fig. 2. The centre part was a prism with a side half the thickness of the original disc and a length of half the diameter of the original disc. The edge part was a ring-shaped body with the annulus thickness less than one tenth of the disc diameter.

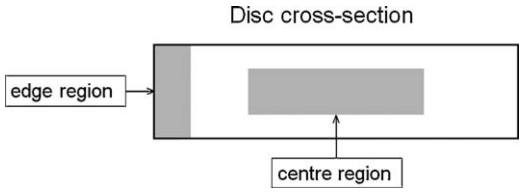

Fig. 2. Schematic drawing of the size and position of test bodies cut out from the gelcast disc.

3. Results and discussion

The graph in Fig. 3 shows mass losses of gelcast discs (diameter 40 mm – thickness 10 mm) immersed in different PEG solutions in dependence on time. The osmotic pressure was kept the same (4.9 MPa) for all solutions. The rate of mass losses and the total removed mass from the gelled bodies increased with increasing molecular weight of polyethylene glycol in the desiccant solution. There was almost a constant value of dewatering with no further change in weight after 6 h of osmotic drying. The maximum mass loss of the gelled body obtained in the solution of PEG 80000 corresponded to the removal of 29% of water content, which was close to the theoretical maximum. The theoretical maximum of water removal during osmotic drying was calculated at 30%. With this water loss, i.e. with the water content being 70% of the original water content in the gelled body, the ceramic particles touch one another and the shrinkage of the body stops. Further water removal would require voids formation in the gelled body, which is energetically unfavourable. However, organic gel located between particles may be stressed and slightly deformed, so the value for maximum water removal during osmotic drying in our gelcast bodies can vary in the range from 30 to 34%. The size of the gelled bodies affected the rate of mass losses but the total mass losses were similar (see Fig. 4). The smaller disc with a higher surface-to-volume ratio showed a higher rate of water removal.

To explain the different water losses in PEG solutions of the same osmotic pressure we must consider the size of PEG molecules. The exclusion limit for a similar acryl amide gel used in protein electrophoresis was reported at about

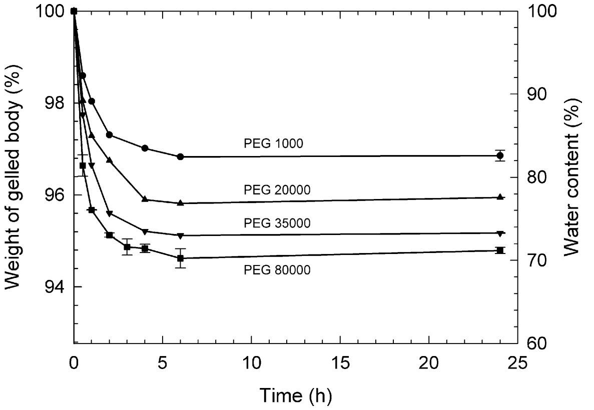

Fig. 3. Mass losses of gelcast disc (dia. 40 mm – thickness 10 mm) immersed in water solutions of PEG with different molecular weights as a function of drying time. The osmotic pressure was kept the same (4.9 MPa) in all desiccants.

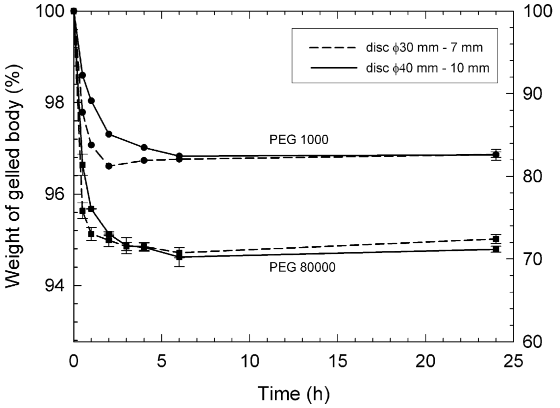

Fig. 4. Mass losses of different discs immersed in water solution of PEG 80000 and PEG 1000 as a function of drying time.

110,000 g/mol,[16] i.e. the molecules with a molecular weight above 110,000 g/mol are so large that they cannot enter the gel pores. For a PEG molecule which is less complex and ordered than a protein, a molecular weight of 80,000 g/mol could be high enough to prevent it from entering the gel pores. PEG molecules with a lower molecular weight were able to enter the gel pores, which decreased the osmotic pressure and finally resulted in lower mass losses. The smaller the PEG molecule, the easier the penetration of the gelled body can be expected. This can explain the lowest water loss (~18%) from the body immersed in the solution of PEG 1000. As will be shown later, the penetrated PEG molecules not only affected the water removal but also affected the pore structure of ceramic green bodies and thus also the sintering behaviour of ceramic bodies. The amount of polyethylene glycol that penetrated the gelled bodies can be determined by comparing the weight losses of air-dried and osmotically dried bodies after organics burnout at 800 °C. The amount of PEG of different molecular weights that penetrated the gelled discs (dia. 40 mm – thickness 10 mm) is shown in Fig. 5. Even for bodies immersed in the solution of PEG 80000 there was a slight PEG uptake (1.29 wt% after 24 h of osmotic drying). Although the molecular weight distribution of PEG 80000 was narrow (a polydispersity index of 1.36), there were still some smaller molecules that were able to penetrate the gel pores. The smaller the molecular weight of a PEG, the higher the absorption determined. The penetration of the smaller disc, i.e. of the disc with a higher S/V ratio, was even higher (4.32% in PEG 1000 and 2.17% in PEG 80000 after 24 h). The PEG molecules continued to penetrate the gelled body steadily even after the water removal stopped. This was the reason for the slight weight increase of small discs after longer times of drying (>4 h), as can be seen in Fig. 4.

Fig. 6 shows the effect of osmotic drying on sintered density of ceramic discs (dia. 40 mm – thickness 10 mm). A decrease in sintered density with drying time in a PEG solution was established. The highest decrease in sintered density was found for the PEG with the lowest molecular weight while a moderate decrease was measured for the PEGs with a higher molecular weight (especially for drying up to 6 h). It was hypothesized that PEG penetration was responsible for the changes in the sintering behaviour of ceramic bodies. The penetrated PEG molecules remained in the pores after drying out of all water and prevented the bodies from uniform shrinkage. The inhomogeneous microstructure with larger pores caused the lower final density of sintered ceramic bodies. The more PEG molecules can enter the body, the worse sintering behaviour can be expected.

Because the PEG molecules penetrated the body from the surface, the microstructure of the surface layer must have been affected by the PEG penetration more than the centre of the body. Fig. 7 shows the difference in green and sintered densities between the centre and the edge region of ceramic bodies. The differences are shown for discs (dia. 40 mm – thickness 10 mm) dried for 24 h in different PEG solutions and compared with the disc dried in air only. The centre part always had a higher density than the edge part. The density differences in green bodies corresponded to the amount of penetrated PEG, so the lowest difference was found in a body dried in PEG 80000. It is interesting to note that a small difference between the green density of the centre and edge region was observed even in the air-dried disc. The same trend in density differences as in green bodies was continued also in the sintered discs. Although the density differ-

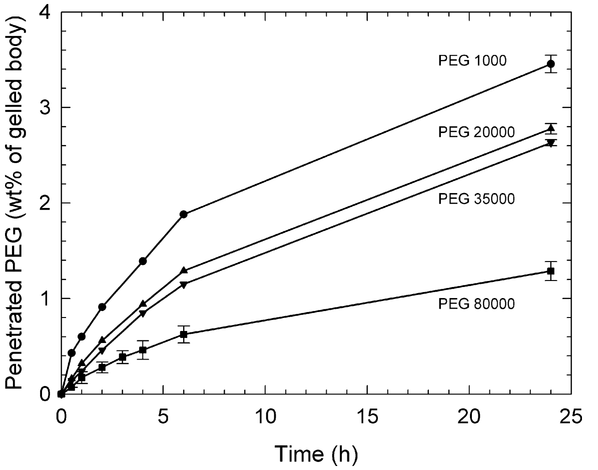

Fig. 5. The amount of PEG that penetrated the gelcast disc (dia. 40 mm – thickness 10 mm) as a function of drying time in liquid desiccant.

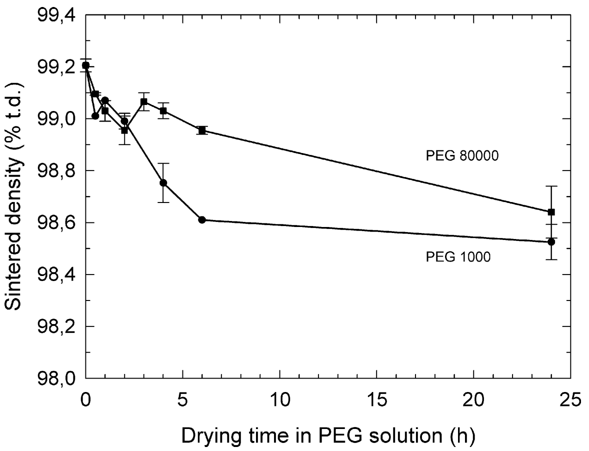

Fig. 6. Sintered density of ceramic disc (dia. 40 mm – thickness 10 mm) as a function of drying time in water solution of PEG 80000 and PEG 1000.

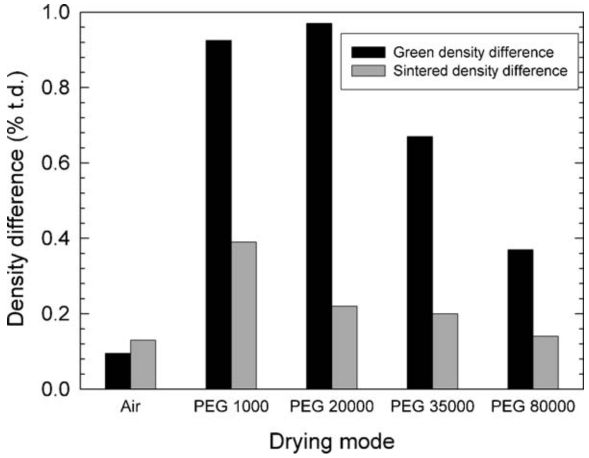

Fig. 7. The differences in green and sintered densities between centre and edge part of gelcast disc after 24 h of osmotic drying in different liquid desiccants. For comparison, the differences in an air-dried disc are also shown.

ence for a body immersed in the solution of PEG 80000 was the lowest among osmotically dried bodies, it was still higher than the difference in the air-dried body. However, the density difference was comparable to air-drying after 4 h of osmotic drying in the solution of PEG 80000, when the water removal was at its maximum already.

The density analyses were confirmed by mercury intrusion porosimetry of the centre and edge parts of discs after gel burnout. Fig. 8 shows the pore size distribution of osmotically dried and air-dried green bodies. The body dried in the solution of PEG 80000 for 4 h had the pore size distribution in the edge part of the disc similar to the pore size distribution in the centre part. The air-dried body had almost the same maximum pore size as in the previous case, nevertheless a slight difference in pore size distribution between the centre and edge part was found. On the other hand the body dried in the solution of PEG 1000 for 24 h showed not only a difference between pore size distribution in the centre and edge part but also an increase in the maximum pore size in both parts.

It follows from the above-mentioned experiments that for successful osmotic drying (i.e. high water removal and uniform sintered density) the polyethylene glycol should have a high molecular weight (≥80,000 g/mol) with a narrow molecular weight distribution to prevent smaller molecules from penetrating the gelled body. For the same reason the time of osmotic drying should be optimized to avoid prolonged drying if not necessary. The main advantage of optimized osmotic drying consists in the fact that the drying step connected with body shrinkage can be controlled and the water excess between particles can be removed uniformly. Fig. 9 shows example of successful utilization of optimized osmotic drying of large alumina body. Osmotic drying followed by air-drying enabled crack-free processing in contrast to the one-step air-drying carried out at room temperature and humidity.

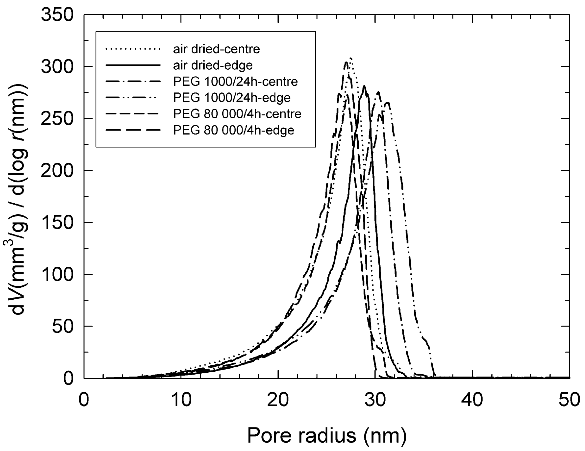

Fig. 8. Pore size distribution in air-dried and osmotically dried green bodies after gel burnout at 800 °C.

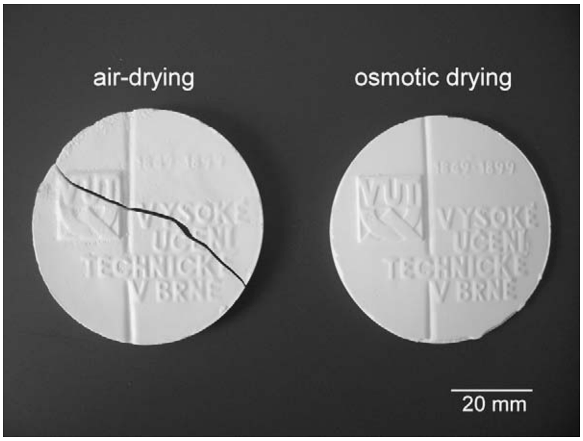

Fig. 9. Images comparing test sample (dia. 60 mm – thickness 4 mm) dried in a liquid desiccant followed by air-drying with sample dried out in air at room temperature and humidity.

4. Conclusions

The water solution of polyethylene glycol with the highest molecular weight was the most efficient liquid desiccant. Up to 30% of water could be removed from gelcast alumina discs during osmotic drying in a 43 wt% solution of PEG 80000. Solutions of polyethylene glycols with lower molecular weights were less effective desiccants because the smaller PEG molecules could penetrate the pores in gelled bodies. The PEG penetration reduced the water removal and resulted in a lower sintered density and an inhomogeneous structure of ceramic body. Optimized drying in the solution of a high molecular weight PEG reduced the penetration and ensured uniform and crack-free drying even in large bodies.

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