Manufacturing of glass components by electrophoretic deposition using nanosized particles

Jan Tabellion and Rolf Clasen
Saarland University, Department of Powder Technology, Im Stadtwald, Geb.43, D-66123 Saarbrucken, Germany

Using nanosized powders, silica and multi-component glasses can be manufactured at significantly reduced temperatures. High-purity silica glass can be sintered to full density at temperatures between 1250 and 1500 °C, depending on the particle size (e.g. Degussa Aerosil OX50, A380). Since shaping is carried out at room temperature, complex-shaped components with structured surfaces can be manufactured. Due to reduced temperatures during processing dopings with lower thermal stability can be incorporated. By means of electrophoretic deposition from aqueous suspensions containing nanosized powders glasses can be prepared fast and cost effective. Thus, a silica green body with a wall thickness of e.g. 10 mm was obtained within 3 minutes. Green bodies of different geometries were produced with controlled green density (≈ 30 to 50 wt-%) and pore size (≈ 6 to 40 nm) and sintered to fully transparent glasses subsequently. A green density up to 84 %TD was obtained by deposition of mixtures of coarse and nanosized particles, without significant increase in sintering temperature. Thus a near-shape manufacture of complex glass components is possible due to the significantly decreased shrinkage of such green bodies.

Introduction

In common manufacturing of silica glasses by melting technology, shaping of components with complex geometry and sharp edges is aggravated by the high temperatures necessary (in the range of 2000 to 2200 °C). Furthermore, at such elevated temperatures the probability of incorporation of impurities is significantly increased. In contrast, production of silica glasses by shaping and sintering of nanosized fumed silica powders enables a near-shape manufacturing of very pure silica glass components[i]. Due to the enhanced sinterability of the nanosized particles, sintering occurs at significantly reduced temperatures as low as 1250 to 1500 °C depending on the powders used (e.g. Degussa Aerosil OX50, A380). Therefore powder manufacturing of silica glasses is a well-established method for optical components, like planar wave-guides or optical fibres[ii,iii]. Manufacturing of silica glasses from nanosized powders combines further advantages compared to common melting technology. Since shaping is performed at room temperature, all conventional shaping techniques known from ceramic manufacturing can be used. Thus, even microstructured silica glass components with complex geometry and sharp edges can be achieved. Furthermore, the open porous structure of the green bodies can be used for a homogeneous or localised doping[iv].

But most of the shaping techniques known from ceramic processing does not fulfill the requirements that arise due to the use of nano-powders. Although dry pressing is widely used for compaction of nano-powders on a laboratory scale, it is not suitable for manufacturing on an industrial scale due to the very low bulk density of nano-powders. Furthermore, dry pressing of nano-powders, which normally show a high degree of agglomeration, usually results in green bodies with poor microstructural homogeneity. This is unfavourable because this inhomogeneity can be found within the sintered glass and furthermore, sintering behaviour is directly related to microstructure[v]. Therefore only suspension-based techniques are suitable for shaping of glass components from nanosized powders. As high a green density as possible combined with a small pore size and homogeneous microstructure is desirable to achieve dense silica glasses with adequate optical

properties. In case of slip casting the deposition rate decreases strongly with decreasing particle size. Furthermore, suspensions with high solids content have to be used, to achieve a sufficient green density. And inhomogeneity within the suspension can result in green bodies with inhomogeneous microstructure.
In contrast, deposition rate is independent of particle size in case of electrophoretic deposition (EPD). Since the electrophoretic mobility of dispersed particles is directly proportional to permittivity, particularly high deposition rates can be achieved by EPD from aqueous suspensions. Furthermore, no severe safety precautions have to be taken and no organic and often hazardous waste has to be disposed. Thus, green bodies can be shaped fast and cost-effective from nanosized particles by means of EPD. Silica glasses could be manufactured with a deposition rate as high as 0.5 $g/cm^2 \cdot min$ from aqueous suspensions of nanosized fumed silica particles[vi]. In contrast to slip casting high green densities can by achieved by EPD from suspensions with relatively low solids content. Due to the low solids content and the high electrostatic stabilisation of the particles, normally adjusted for EPD, very homogeneous green bodies with narrow and monomodal pore size distribution are obtained. Green density and pore size distribution of such silica green bodies can be tailored by adjusting the processing parameters[vii].
But the manufacturing of silica glass components from nano-powders is complicated by the high intrinsic shrinkage of the resulting green bodies during sintering (up to 43 % linear shrinkage). Thus, near-shape manufacturing is not possible and sophisticated drying and sintering programs have to be carried out to avoid cracking or deformation, especially for larger components. By using mixtures of nanosized fumed silica particles and coarser silica glass powders a minimisation of the shrinkage during drying and sintering is possible. Green bodies with very high green densities up to 80 % of the theoretical value could be achieved by casting of aqueous suspensions of such powder mixtures with optimised particle size distribution[viii]. But the solids content of the suspensions has to be very high (high viscosity) to avoid separation of nanosized and coarser particles during casting and drying. Due the high viscosity the removal of gas bubbles from the suspension is difficult and the resulting sintered glass often shows poor optical properties. In contrast, no particle separation occurs during electrophoretic deposition because there is no dependency of electrophoretic mobility from particle size as mentioned above. Comprehensive reviews about EPD as shaping technique for ceramics can be found in[ix,x].

Experimental set-up

Aqueous suspensions of both nanosized and coarser silica powders were prepared for electrophoretic deposition. The nanosized fumed silica powders used were Degussa Aerosil OX 50 and A380 with a mean particle size of 40 and 8 nm respectively. The average size of coarser silica particles was about 10 to 30 μm. The different silica powders were dispersed gradually in bidistilled water under constant torque by means of a dissolver. Vacuum was applied to avoid the incorporation of air bubbles into the suspension. To achieve an electrostatic stabilisation of the particles and to adjust the ζ-potential, different amounts of tetramethylammoniumhydroxide (TMAH) were added. Suspensions with different solids content, from 10 to 50 wt-% for nanosized fumed silica powders and up to 70 wt-% for powder mixtures were used. Rheological behaviour of the suspensions was investigated by rotational viscosimetry and ζ-potential of the silica particles was measured by means of a Zeta-Sizer (Malvern). In Addition electrical conductivity and pH were measured to guarantee reproducibility.

Electrophoretic deposition was carried out under constant applied voltage based on the membrane-method[xi], where the electrophoresis cell is subdivided by an ion-permeable membrane into two chambers. Thus, deposition of particles (onto the membrane) and recombination of ions (at the electrodes) were separated and no gas bubbles occurred within the deposit. One chamber was filled with the suspension, the other with bidistilled water and TMAH where necessary. The width of the different chambers was optimised after measuring the effective electric field strength within the electrophoresis cell[xii].
After shaping, the green bodies were dried in air under ambient humidity; no cracking occurred. Green density of the deposited compacts was determined according to Archimedes method and pore size distribution was measured by mercury porosimetry. Sintering of the compacts was carried out either under vacuum, atmosphere or in a zone-sintering furnace at temperatures between 1250 and 1550 °C depending on the powders used and the deposition parameters.

Results and Discussion

Suspensions with different amount of a nanosized fumed silica powder (OX50) were prepared and electrophoretically deposited as described above. The influence of solids content on deposition rate, green density and solids content was investigated as a function of the parameters of the EPD. Figure 1 shows the deposition rate ($g/cm^2 \cdot min$) as a function of OX 50 content and applied electric field. The suspensions used were stabilised by 0.75 wt.% TMAH correlated to the amount of OX50. It can be seen that the deposition rate increases both with increasing solids content of the suspension and applied electric field. Thus, depositing a suspension with e.g. 30 wt % OX50 electrophoretically at 6 V/cm a deposition rate of ≈ 0.16 $g/cm^2 \cdot$ was measured. As a result a green body with a wall thickness of 10 mm and a green density of 39 % of the theoretical value was achieved within 5.5 minutes.

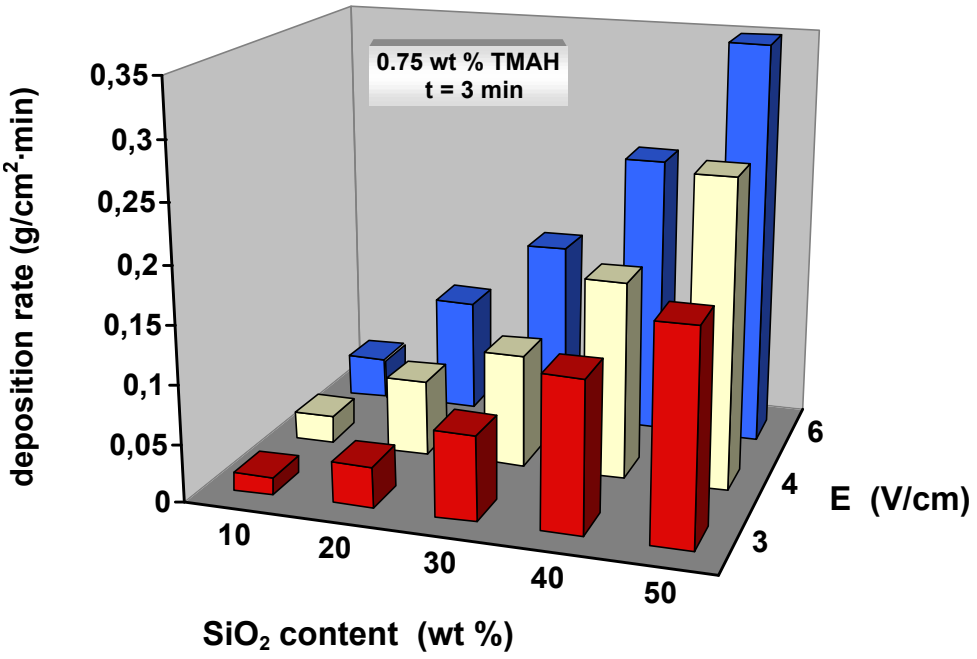

Figure 1: Deposition rate as function of silica (OX50) content within the suspension and applied electric field during EPD

Furthermore, the influence of important process parameters like applied electric field, pH and solids content of the suspensions on pore size distribution and green density (measured by Archimedes method) was investigated. All green bodies shaped by EPD showed a narrow monomodal pore size distribution (measured by mercury porosimetry). Green density and mean pore size of OX 50 green bodies prepared by EPD from aqueous suspensions with different solids content are given in table 1.

wt % OX50	10	20	30	40	50
green density (% TD)	35,9	36,3	39,5	43,5	46,6
mean pore size (nm)	37	37	35	22	19

Table 1: Relative density and mean pore size of electrophoretically deposited silica green bodies as function of OX50 content (t = 3 min; E = 3 V/cm, 0.75 wt % TMAH)

In figure 2 some silica green bodies are shown that were electrophoretically deposited from an aqueous suspension of a mixture of nanosized OX50 and coarser particles. A comparably low solids content of 65 wt % was chosen to guarantee a low viscosity and thus a good homogeneity of the suspension. On the basis of SEM images no separation in terms of size could be found. It could be shown earlier, that by optimising the ratio of small and bigger particles the linear shrinkage during sintering can be decreased down to 7 %[8].

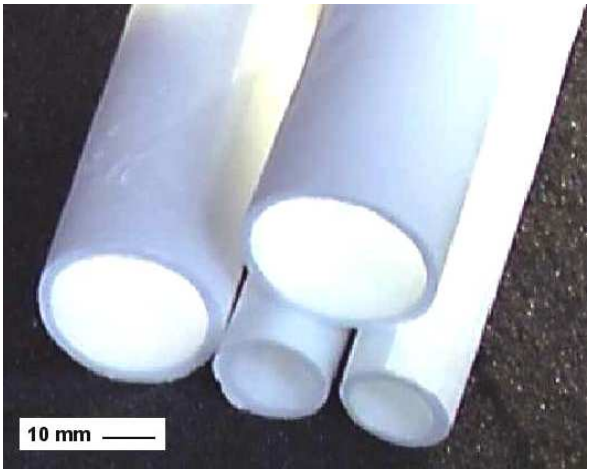

Figure 2: Electrophoretically deposited silica (mixture OX50/coarse) green bodies

The sintering behaviour of silica green bodies shaped by EPD and colloidal gel method from different powders with different particle size is compared in figure 3. Furthermore, a small silica glass sample is shown that was electrophoretically deposited from an OX50 suspension with 30 wt % solids content and sintered at 1320 °C. First, the influence of particle can be seen. The smaller the particle size, the lower the sintering temperature, with a minimum for Degussa A380 (8 nm) of 1250 °C.

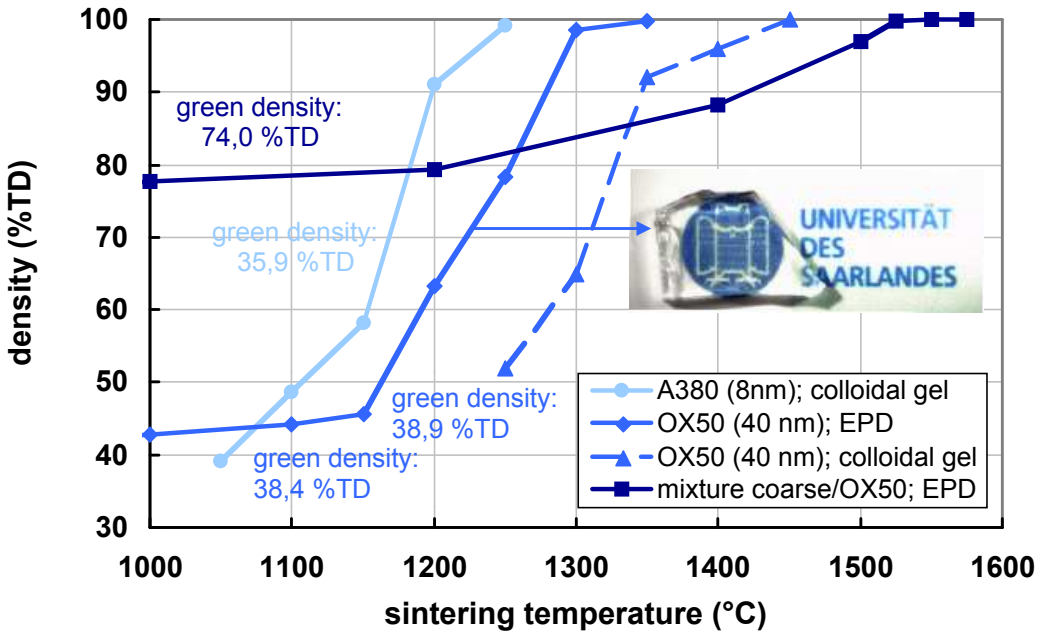

Figure 3: Sintering behaviour of silica green bodies shaped by EPD and colloidal gel method from different powders and small silica glass sample (OX50) formed by EPD

Furthermore, it can be seen that the shaping technique has an important influence on sintering behaviour. The OX50 sample prepared by EPD can be sintered to a fully dense, transparent silica glass at 1320 °C, whereas in the case of the sample shaped by colloidal gel method a sintering temperature of 1450 °C is necessary. Since this is not related to a difference in green density, the discrepancy in sintering temperature is due to the more homogeneous structure of the EPD sample.

Conclusions

By means of electrophoretic deposition of nanosized fumed silica particles from aqueous suspensions complex shaped silica glass components can be manufactured on a competitive scale. Green bodies with a wall thickness of 10 mm can be deposited within less than 5 minutes. Density and pore size of the green bodies can be tailored by adjusting the parameters of the EPD. Such green bodies can be sintered to fully dense and transparent silica glasses at about 1250 to 1350 °C. Sintering temperature is decreased compared to colloidal gel method in the range of about 100 °C. By electrophoretic deposition of mixtures of nanosized and coarser silica particles green bodies with homogeneous microstructure and high density could be prepared that showed a very low shrinkage of about 7 to 10 %. As a result near-shape manufacturing of complex geometries is possible at sintering temperatures of about 1450 to 1550 °C, depending on the ratio of nanosized to coarser particles.

---

[i] R. Clasen, J. Non-Cryst. Solids **89**, pp. 335-344 (1987).

[ii] J. B. MacChesney and D. DiGiovanni, J. Am. Ceram. Soc. **73**, pp. 3537-3555 (1990).

[iii] R. Clasen in *Fundamentals of Glass Science and Technology,* 1997, (Glass Research Institute, Växjö, Sweden, 1997), pp. 166-173.

[iv] J. Tabellion, K. Smeets and R. Clasen, Key Eng. Mater. **206-213**, pp. 2069-2072 (2002).

[v] L. Bergström, K. Shinozaki in *Fourth Euro Ceramics - Vol 2: Developments in processing of advanced ceramics,* 1995, edited by C. Galassi, (Gruppo Editoriale Faenza Editrice, Italy), pp. 3-14.

[vi] R. Clasen, in *Science, Technology and Applications of Colloidal Suspensions*, edited by J. H. Adair, J. A. Casey, C. A. Randall, S. Venigalla (Am. Ceram. Soc., Westerville, USA, 1995), pp. 169-184.

[vii] J. Tabellion, R. Clasen, in *Innovative Processing and Synthesis of Ceramics, Glasses and Composites IV*, edited by N. P. Bansal, J. P. Singh (Am. Ceram. Soc., Westerville, USA, 2000), pp. 185-196.

[viii] R. Clasen, Key Eng. Mater. **206-213**, pp. 235-238 (2002).

[ix] M. S. J. Gani, Industrial Ceramics **14**, pp. 163-174 (1994).

[x] P. Sarkar and P. S. Nicholson, J. Am. Ceram. Soc. **79**, pp. 1987-2001 (1996).

[xi] R. Clasen in *2nd Int. Conference on Powder Processing Science,* 1988, edited by H. Haussner, G. L. Messing, S. Hirano, (DKG, Köln, Germany, 1988), pp. 633-640.

[xii] J. Tabellion, R. Clasen, in *Innovative Processing and Synthesis of Ceramics, Glasses and composites IV*, edited by N. P. Bansal, J. P. Singh (Am. Ceram. Soc., Westerville, USA, 2000), pp. 197-208.