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Simulation and investigation of pore size graded titania layers during sintering

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The topic of this work is the investigation of the sintering process of thin self-supporting ceramic layers with a gradient in the particle size and pore size distribution. These graded titania layers were produced by centrifugal deposition from mixed sol powder mixtures with wide particle size distributions. The graded structure causes strong deformations of the layers during the drying and the sintering step. Finite element simulations were used to describe the deformation behaviour during sintering. The results were compared with the parpage of real layers. Furthermore, a possibility to suppress a sintering deformation is shown with the help of experimental and simulated data. The sintered layers were characterized by SEM, AFM, gas adsorption and roughness measurements. Quantitative image analysis of polished cross-sections and AFM investigations of ion beam cutted slopes were used for detecting the run of the pore size gradient within the layers.

1. Introduction

Ceramic layers with a continuous gradient in the pore size distribution offer two advantages in comparison to layers with a stepwise decrease in the pore diameter, which are usually used as filtration membranes. First, layers with a continuously graded pore structure can be produced in only one processing step, whereas the conventional asymmetric membranes are built up step by step. Starting with a tubular or planar ceramic support with a pore size of about 10 μm, several coatings with decreasing particle and pore size are deposited up to the top coating with the finest pore size, which may be as small as a few nanometers. In practice up to five layers in the microfiltration regime are used, completed by several coatings at the top with similar particle size for the ultrafiltration range and, eventually, additional coatings for nano-filtration [1]. Each coating must be deposited, dried and sintered separately.

Second, the thickness of the graded layers can be reduced, because in this case coatings with intermediate pore size are unnecessary. A thinner membrane layer can achieve the same separation performance, but at a higher production rate due to the reduced flow resistance [2].

A possible route to the preparation of ceramic layers, tubular or planar, with a graded pore structure is given by centrifugal deposition techniques. Joensson *et al*. [3] describe the production of cylindrical bodies made of Cr-Ni-steel powders showing a gradient in the pore size in a range of some microns. Tubular ceramic membranes with a thickness of 5 mm and a graded pore structure between 40 and 250 nm were produced via centrifugal deposition by Hong [4].

Besides centrifugal deposition other techniques are used to achieve a gradient in pore size and porosity. Cichocki *et al*. [5] produced ceramic preforms with a graded porosity via colloidal infiltration of moulded polymer sponges, followed by pyrolysis and sintering. Planar discs of α-alumina (4–7 mm in thickness) with a graded pore structure were obtained by slip casting using colloidal suspensions of wide particle size distributions [2].

The general goal of this work was to develop planar, self-supporting titania layers thinner than 1 mm showing a gradient in the pore size distribution in a range between several microns and a few nanometers by means of centrifugal deposition. Three fundamental requirements must be satisfied to achieve the desired gradient in the sediment:

- The particle size distribution of the suspension must be very wide to obtain a pore size gradient in a wide range.

TABLE I Characteristic data of the titania powders and the titania sol used

Powder	BET/ $[m^2/g]$	Particle size/microns d_{10}	d_{50}	d_{90}	Isoelectirc point	Phase content
TiO_2 R-1053[a]	3.3	0.34	0.68	1.22	pH 5.0	Rutile
TiO_2 P 25[b]	48.3	0.11	0.18	0.3	pH 6.5	Anatase + rutile
TiO_2-sol	308	<0.02	0.045	0.1	—	Amorphous

[a]Kronos-Titan.
[b]Degussa.

- The solid content of the suspension must be very low to prevent a collective motion of the particles in the centrifugal field, i. e. the conditions for particle size segregation must be fulfilled.
- In contrast to the slip casting technique [2], the suspension must be stable against flocculation. The reason is, that the suspension contains particles differing in their diameters enormously (40 nm to 3 microns). Therefore, the attractive van der Waals forces between the large powder particles and the small sol particles would cause a rapid flocculation in absence of stabilization and a particle size segregation would be prevented.

A sufficient stabilizing effect was attained by using a sterically stabilized titania sol. A detailed description of stabilizing sol-powder mixtures as a basic requirement for the preparation of thin layers with a pore size gradient by centrifugal deposition is given in [6].

The preparation of the graded layers is associated with numerous technological difficulties. One problem during drying and sintering is the strong tendency of the layers to warping and crack formation. In this work the sintering behaviour of the above-mentioned titania layers is investigated. By means of the finite element method (FEM) the warping is simulated and the results are compared with sintering experiments.

2. Experimental

Two commercial titania powders were dispersed in water in various ratios. Both powders showed different particle size distributions. The characteristic powder data are shown in Table I. To achieve a high double layer repulsion the pH-value of the dispersion was adjusted to 12, far from the isoelectric points of the powders. After this, up to 10 wt.-% hydroxyethyl cellulose acting as a temporary binder in the sediment and the sterically stabilized TiO_2-sol were added to the suspension. The preparation of the sol was described in detail in [6]. The layers were deposited on circular alumina plates with a centrifugal acceleration of 4,000 g applied for 90 min.

Such a procedure leads to the following structure of the deposited layer. The bottom of the sediment reflects the complete multimodal particle size distribution of the suspension. With increasing thickness the distribution shifts to smaller values and the top of the sediment is formed only by the finest sol particles which can be settled in the centrifuge. In this way it could be achieved that finer particles showing a much higher sintering activity than the large powder particles are present in the entire layer, whereas the large particles are concentrated only in the lower part of the sediment. This fact should help to reduce the gradient in the sintering activity over the thickness of the layer.

The sediments were removed from the centrifugal tubes and supercritically dried. This drying technique

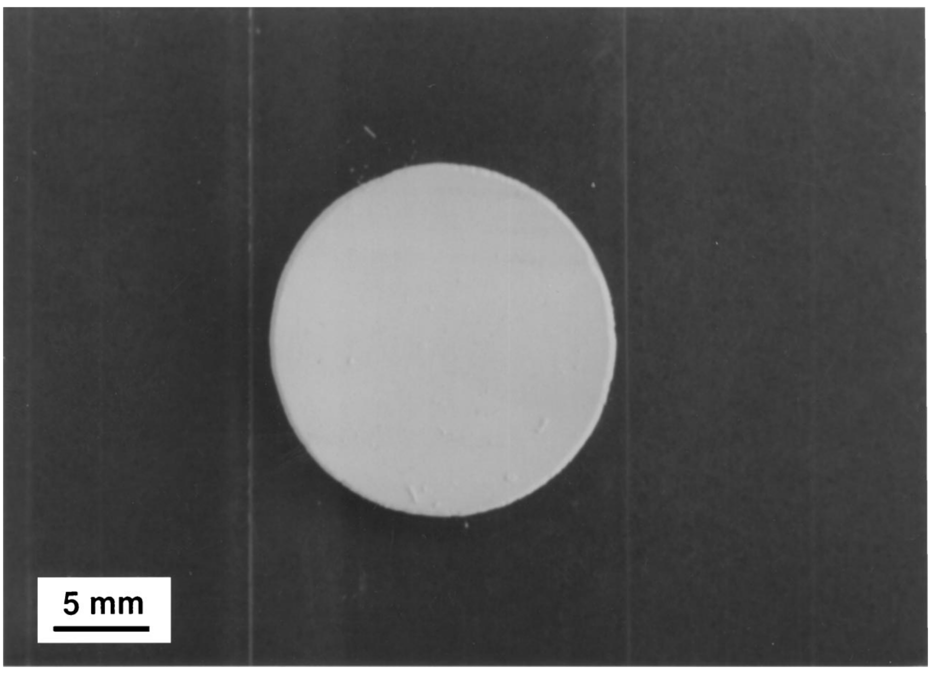

Figure 1 Supercritical dried titania layer with a gradient in the pore size distribution.

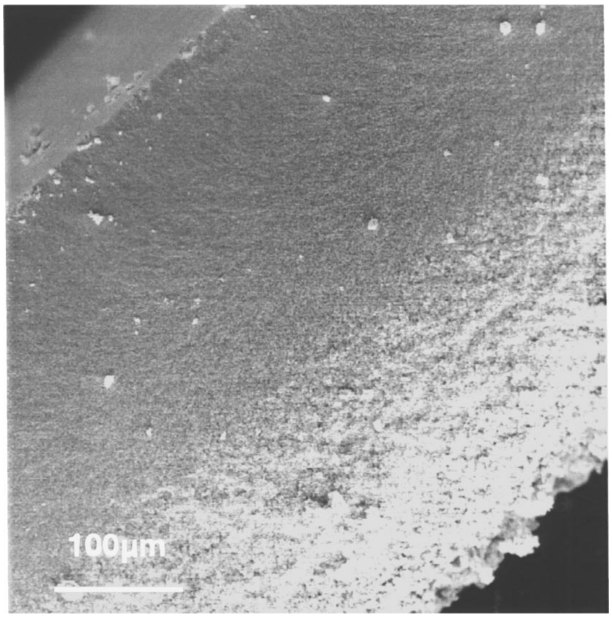

Figure 2 SEM micrograph of a fracture surface of a graded titania layer.

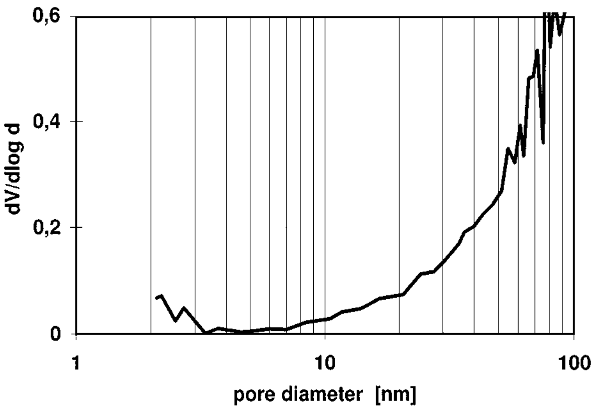

Figure 3 Pore size distribution of a sintered titania layer with a pore size gradient (calculated by the BJH-method from nitrogen adsorption data).

excludes capillary forces by preventing a direct liquid/vapour transition. Supercritical drying was the only drying method to get planar, defect-free graded layers as shown in [7].

The specimens were sintered in electrical furnaces at temperatures up to 1200 °C and different hold times. In some cases an alumina disc was laid on the specimens during sintering in order to suppress the warpage. The planarity of a dried layer was measured with a roughness measuring device (Perthometer). Furthermore, the samples were investigated by SEM and quantitative image analysis. The burn-out of the organic additive hydroxyethyl cellulose during the heating process was characterized by differential thermoanalysis (DTA) and thermogravimetry (TG).

3. Results and discussion

Figs 1 and 2 show a supercritically dried graded titania layer consisting of 35 wt.-% coarse powder, 65 wt.-% fine powder and sol and a SEM fracture surface of this sample, respectively.

Owing to the exclusion of capillary forces during drying the layers were smooth and planar. Fig. 2 gives an impression of the achieved gradient in the particle size of the layer. The smallest particles which were deposited under the applied settling conditions where 40 to 80 nm in diameter. These data were measured by SEM and AFM-investigations of the layer surface. From these particle diameters pore sizes between 8 and 16 nm at the top of the sediment are expected. However, the nitrogen adsorption data pointed to much smaller pores down to 2 or 3 nm, which are attributed to an internal porosity of the deposited sol particles.

The criteria for choosing the sintering temperature are that the sintering temperatures must be high enough to give the layer a sufficient mechanical strength and wear resistance, but low enough to keep the pore

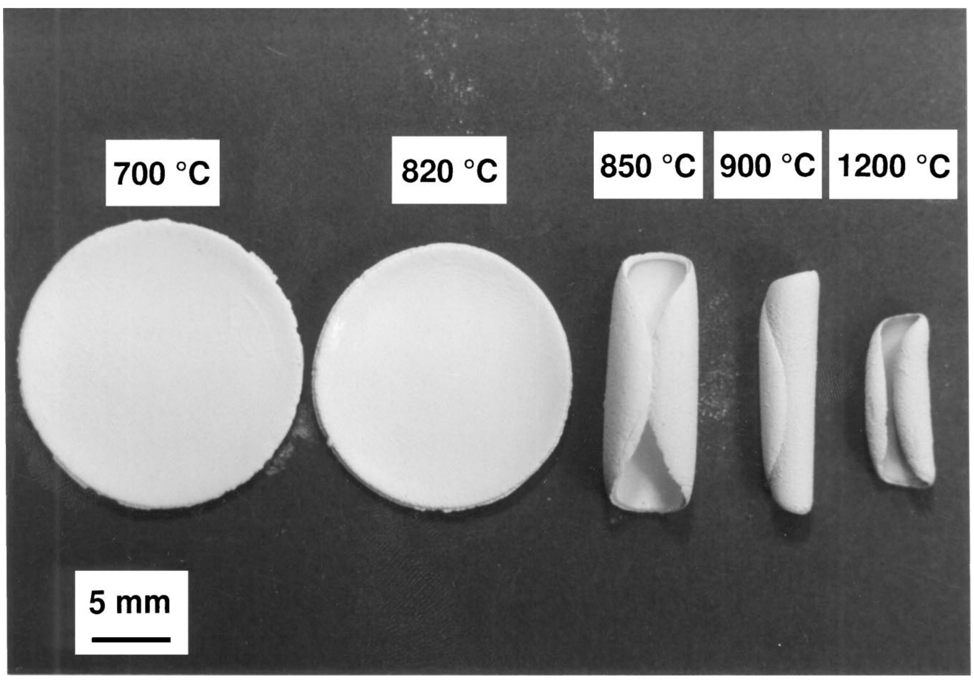

Figure 4 Influence of the sintering temperature on the deformation of the graded layers.

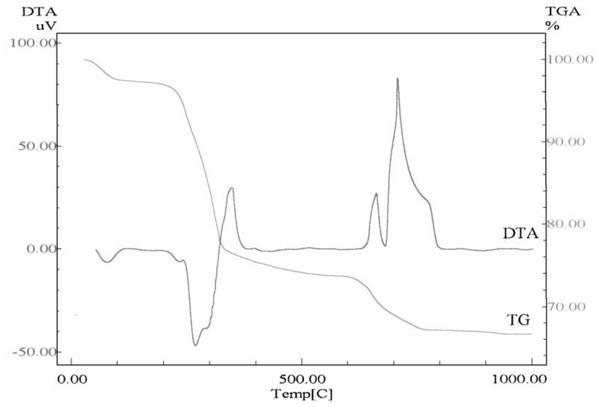

Figure 5 DTA- and TG-curves of the decomposition behaviour of hydroxyethyl cellulose.

structure open. Up to 800 °C practically no sintering occurred. The best compromise appeared to be a sintering temperature of 850 °C, where the layers acquired sufficient mechanical strength and still had enough open porosity as demonstrated by the nitrogen adsorption data obtained from the BJH method (Fig. 3). At higher temperatures the pore structure began to change. With increasing sintering temperatures a strong deformation of the graded layers was observed (Fig. 4). In spite of the presence of finest particles not only in the upper part of the sediment, but also in the coarse-grained lower part, the sintering rates of the different grain mixtures over the thickness are substantially different.

Surprisingly, very fine pores of only a few nanometers still exist up to the applied sintering temperatures of 850 °C. Normally, these smallest pores, which were attributed to an internal porosity of the sol particles, are expected to disappear faster than larger pores and at lower temperatures. A possible explanation for the inhibited sintering activity was obtained by DTA- and TG-measurements of the burn-out of the hydroxyethyl cellulose, which acted as a temporary binder in the sediment (Fig. 5). The DTA- and TG-curves allow to suggest an amount of carbon remaining in the layer after the decomposition of the binder around 300 °C. This residual carbon was removed at temperatures between 700 and 800 °C and may have a negative influence on the sintering kinetics of the finest particles. In the case of the graded layers a delayed sintering has the advantageous effect that the layers can be sintered at higher temperatures resulting in an improved strength.

A significant change in the deformation behaviour could be achieved when varying the coarse/fine powder ratio in the suspension. In this way the pore size and the particle size gradient in the sediments was changed, too (Fig. 6). The warping increased as the thickness of the fine-grained part of the layer increased compared to the thickness of the coarse-grained part. Layers which were deposited from suspensions containing only the coarse powder or the fine powder did not show any deformation during sintering.

To prevent the deformation of the graded layers, they were covered by alumina discs ($m = 3.2$ g) similar to those used during centrifugation. These discs did not constrain the radial shrinkage of the sediments, but they permitted the production of quite smooth and plane layers (Fig. 7). An alumina disc with a smaller weight ($m = 2.133$ g) was not sufficient to suppress the warpage and deformation completely. Fig. 8 shows the deformation of such a sample measured by means of a roughness testing device. The deformation was circular symmetric with the rim and the centre warping upwards. The surfaces of the sintered samples were investigated by SEM (Fig. 9). The micrographs did not show any great defects.

Two different measuring methods were used to detect the expected pore size gradient in the sediments: quantitative image analysis of SEM-micrographs and AFM-investigations. A detailed description of the characterization is given in [8]. Fig. 10 shows the dependence of the pore size in a sintered layer on the position in the sediment. The pore size is measured by quantitative image analysis in the coarse-grained part and by AFM in the fine-grained part.

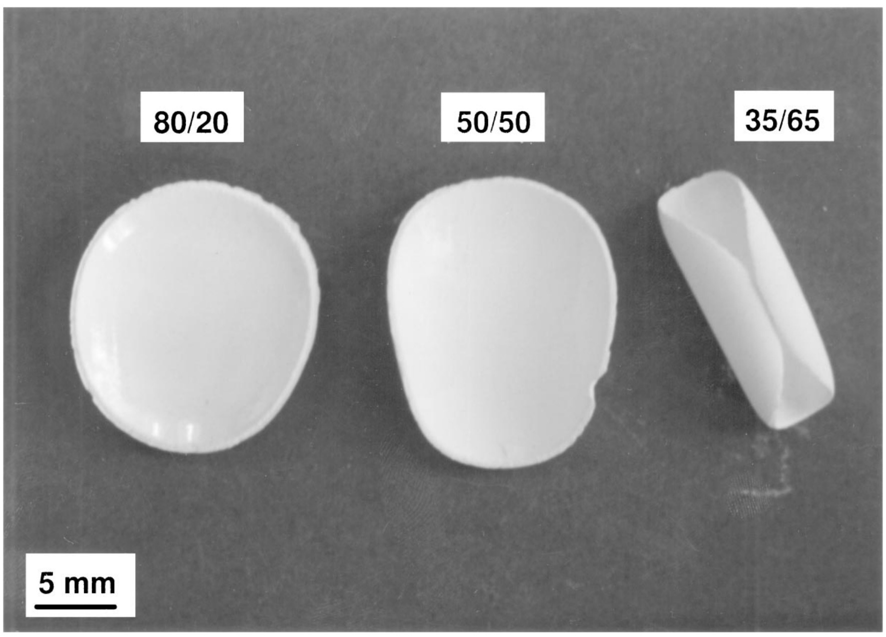

Figure 6 Influence of the coarse/fine powder ratio in the layer composition on the deformation behaviour during sintering at 850 °C for 10 minutes.

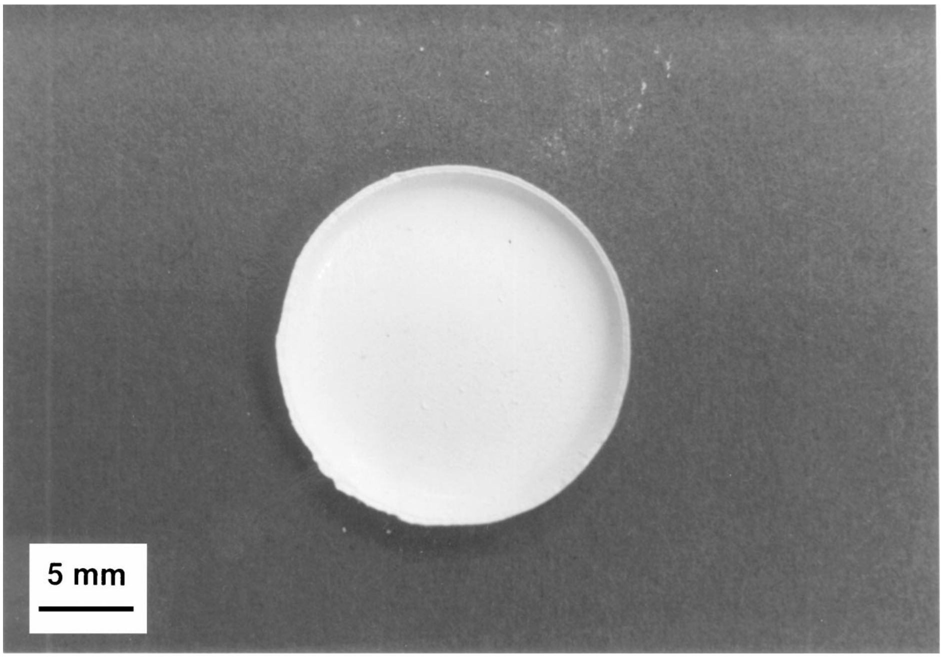

Figure 7 Graded titania layer after sintering at 950 °C (warping was reduced by covering with an alumina disc).

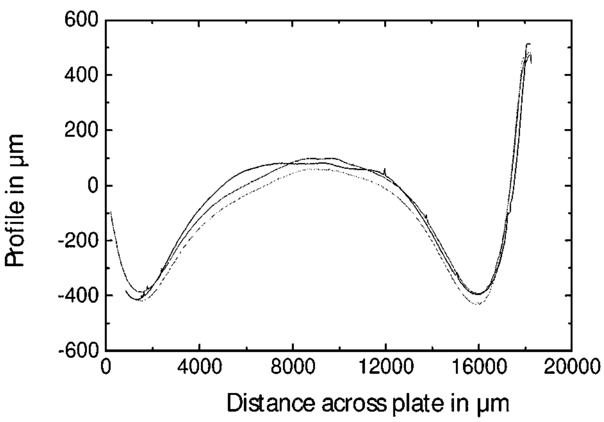

Figure 8 Profile of a sintered layer covered with an alumina disc (weight = 2.133 g) measured in a roughness testing device.

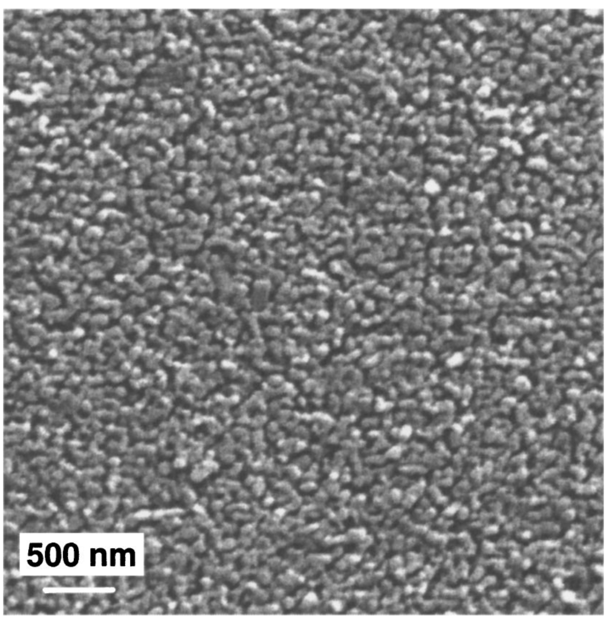

Figure 9 SEM micrograph of the top of a sintered graded layer.

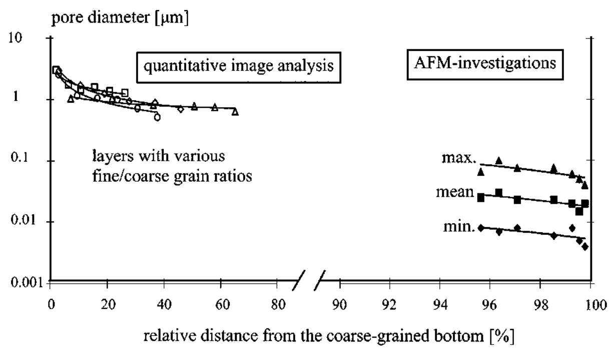

Figure 10 Dependence of the pore size in a sintered layer on the position within the sediment.

3.1. FE-simulation of the deformation behaviour during sintering

The warpage of the graded components during sintering was modelled using the finite element method. The calculation is based on a constitutive model for solid state sintering as described in [9]. Its general form is

$$\dot{\varepsilon}_{ij} = \frac{\sigma'_{ij}}{2G} + \delta_{ij}\frac{\sigma_m - \sigma_s}{3K} \quad (1)$$

where $\dot{\varepsilon}_{ij}$ is the strain rate tensor, σ'_{ij} is the deviatoric stress, σ_m is the mean (or hydrostatic) stress, δ_{ij} is the Kronecker symbol, G and K are the shear and bulk viscosity, respectively, and σ_s is the sintering stress. The material parameters G, K and σ_s depend on temperature, density and grain size. Here, the dependence on grain size is important. For solid state sintering by grain boundary diffusion, this dependence is given by G and $K \propto d^3$, and $\sigma_s \propto 1/d$. Hence, coarse grained material has a much higher resistance against sintering and a smaller sintering stress than fine grained material.

This material model is implemented as a user defined material routine into the finite element code ABAQUS [9]. To simulate the sintering of the graded titania plates approximately, a circular plate with 22 mm diameter and 0.85 mm thickness is discretized by 20-noded brick elements. The thickness is divided into four equally thick layers in which the particle size is assumed to be 700 nm, 350 nm, 140 nm and 70 nm (from bottom to top). The green density is assumed to be 0.56 in all layers. For the expected symmetry of the warped plate, only a quarter of the disc needs to be modelled.

Fig. 11 shows a time sequence of the warping of the plate. Since the fine grained layer sinters first, the plate bends upwards. Initially the warpage remains axial symmetric, but at larger deformation a bifurcation occurs, and the deformation continues in a mode with lower symmetry. An analogous bifurcation is observed, when plates with a gradient in the thermal expansion coefficient are cooled or heated [10]. Besides showing the deformation of the plate, Fig. 11 is also a contour plot of the relative density. At the maximum of the deformation the fine-grained layers are sintered to full or nearly full density. If the sintering is continued for very long times, also the coarse-grained layers start to densify. Fig. 11c shows that then the warpage is reduced and finally changes its sign and the direction of the principal curvature. This stage is not observed in the experiments.

Finally, the experiments with sintering under an alumina disc with a weight of 2.13 g was simulated. In this case the grain size in the four layers is assumed to be 700 nm, 100 nm, 70 nm and 70 nm in order to approximate the conditions in a 35/65 disc using the previous finite element mesh with four layers. The applied weight is not enough to suppress the warpage completely, but it suffices to suppress the bifurcation mode of deformation. The deformation remains axisymmetric, but now not only the rim but also the centre of the plate move upwards (Fig. 12). This is consistent with the experimental result (Fig. 8).

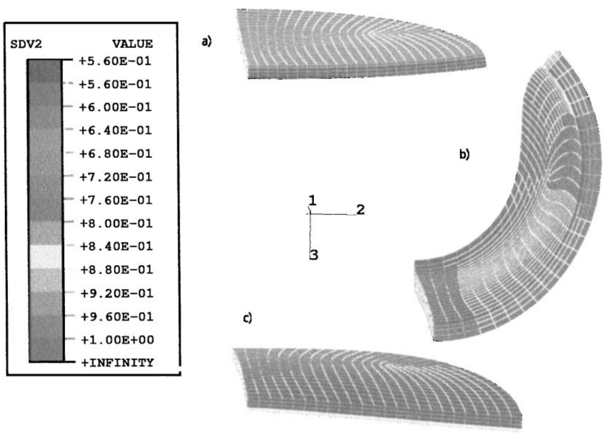

Figure 11 Warping of a plate with a grain size gradient: fine-grained material in the top layers sinters first. SVD2 is the relative density. Only a quarter of the plate is shown. a) initial sintering stage; b) maximum of deformation; c) deformation in the stage of complete densification after long sintering times.

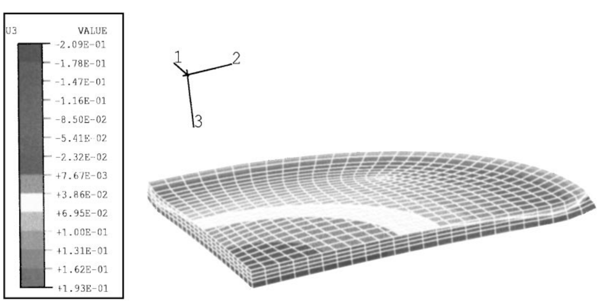

Figure 12 Warping of a plate with a grain size gradient under a weight of 2.133 g. U3 is the displacement in 3-direction.

4. Conclusions

Thin titania layers with a gradient in the pore size distribution were produced by centrifugal deposition. Numerous technological problems had to be solved during the development of these graded sediments. A main difficulty was to prevent the deformation occurring in the sintering step. The deformation behaviour was investigated by sintering experiments and by the finite element method. The results of this simulation showed a good qualitative correspondence with the experimental data. To keep the desired pore structure, the sediments were not fully densified, but showed a strong tendency to warp. This negative effect could be successfully excluded by covering the sediment with an alumina disc during the sintering step.

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