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Electrophoretic deposition applied to ceramic dental crowns and bridges

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Abstract Electrophoretic deposition (EPD) was used as shaping technique for ceramic dental crowns and dental three-unit and four-unit bridges in the high loaded molar region. Because of esthetical aspects and their biocompatibility ceramics are the material of choice for dental applications. Allergic reactions or toxic tissue damages can be prevented largely by application of ceramic dental products. Zirconia in its tetragonal yttria stabilized polycrystal form (TZP) and alumina toughened zirconia (ATZ) offer highest strength combined with highest toughness. In this publication, the influence of the kind and the amount of dispersing agent on the rheological properties of the ceramic suspensions was investigated. For EPD plaster stumps which had been prepared for the dental crowns and bridges by the dental technician were coated with silver and were directly used as deposition electrodes. For optimisation of the removing step of the deposited crown or bridge cap from the plaster stumps organic temporary binders and organic intermediate layers were investigated. The dental parts were sintered either to full density or to porous ceramics for a subsequent glass infiltration step.

Introduction

Electrophoretic deposition (EPD) is known as a colloidal process wherein ceramic bodies are shaped directly from a stable colloid suspension by a DC electric field [1]. EPD offers the possibility to shape ceramic powders to densely packed homogeneous green bodies. It essentially consists of two steps: in the first step, electrically charged particles suspended in a liquid are forced to move toward an electrode, and in the second step, the particles collect at one of the electrodes and form a coherent deposit on it [1, 2]. Charging of the suspended solid particles may occur through selective dissolving of ions and/or through adsorption of ionic compounds onto the surface of the solid particles, creating an electric double layer at the surface of the solid particles. The electric double layer serves a double function: to stabilize the suspended particles and to allow movement of the particles in an electric field [3]. The reaction mechanism in electrophoretic body formation results in an arrangement of individual particles, which is conductive to the formation of homogeneous green bodies with monomodal pore radii distribution [4, 5]. Obviously, the shaping process is followed by a densification step such as sintering in order to obtain a fully dense material. Main factors for electrophoretic shaping of ceramic bodies

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are the dielectric constant of the suspension, the suspension viscosity, the electrical field strength, and the zeta potential of the powder particles [6]. A high dielectric constant of the suspension media causes a high velocity of particle migration and in this way an increased mass transport. Equally, a high zeta potential is necessary for the mass transport such as for the bulk shaping process itself. A necessary but not sufficient condition for a high zeta potential is a high surface charge [1]. However, the greatest problems in technical use of EPD cause controlling of the geometry of the electrical field, corrosion of the electrodes and gas bubble formation owing to electrolysis such as humidity gradients especially in thicker deposits which are the limiting factor for the wall thickness of ceramic components [4]. The use of organic liquids as suspending media for the EPD of powders overcomes some of the problems associated with deposition from aqueous suspensions, namely those of gas formation from the electrolysis of water and anodic corrosion. The green density of deposits formed from non-conducting powders with a small particle size range is normally about 60% of the theoretical density which indicates that the particles are closely packed in the deposit after drying [7]. Little is known about the structure of the green deposit while still in the suspension. In general, one needs to take into account that the deposit is saturated with liquid and that some shrinkage has to be accommodated during drying. For free standing objects, the adhesion between the electrode and the part should be minimal so that they can be easily separated [8].

EPD has been applied for producing coatings, for shaping monolithic, laminated and graded free-standing objects, and for infiltration of porous materials and woven fiber preforms for composite production [1].

All-ceramic dental bridges are exceedingly desired for the use in the high loaded molar region of teeth restorations. For the production of high-performance ceramics for dental applications a shaping method is required which is capable of producing homogeneous, low-stress green bodies. At present, following methods for metal-free ceramic restoration are used: coating of a model tooth stump with a slurry, compacting of ceramic powder under thermal treatment, direct ceramic machining (DCM) [9], and EPD combined with subsequent pre-sintering and glass infiltration [10].

Experimental

Characteristic data of the initial powders which were used for the EPD of ceramic dental crowns and bridges are shown in Table 1.

For preventing electrolytic decomposition of water at the electrodes during the EPD water-free ethanol was used as suspension media. Since EPD requires charged particles, various organic dispersants (polyacrylic acid MW 2000 (Sigma-Aldrich), diethylamine (Merck), polyethylene imine (Sigma-Aldrich), benzoic acid (Merck), 4-hydroxybenzoic acid (Riedel-de Haen)) were investigated by zeta potential measurements (ZetaProbe, Colloidal Dynamics, Australia/U.S.). The suspensions with solid contents of 50 wt.% and 60 wt.%, respectively, were prepared by stirring under ultrasonic treatment and characterized by measurements of the dynamic viscosity. The EPD of dental crowns and bridges was carried out directly onto the plaster stumps prepared by the dental technician. For that reason, the stumps had to be made electrical conductive, and a thin film of conductive silver was painted onto the plaster stumps (Fig. 1).

The plaster stump was contacted with a ribbon of copper from the bottom site. A sheet of platinum acted as counter electrode for the deposition. In the case of the dental bridge a thin wax bar was positioned in the tooth gap and treated in the same way as the plaster stump (Fig. 2). The EPD was carried out in an EPD cell with a content of 250 ml suspension at a constant DC voltage of 30 V for 10 min and 15 min, respectively. These parameters had shown to be the most effective for attaining crown caps with sufficient thickness and stability. For the EPD experiments with the dental bridges the deposition time was increased to

Table 1 Characteristic data of the initial powders

Type of powder	Producer	Composition [wt.%]	Particle Size [μm]	BET Surface [m^2/g]
TZ-3Y (TZP)	TOSOH Corp., Japan	Y_2O_3 = 5.12 Al_2O_3 = 0.005 SiO_2 = 0.07	d_{50} = 0.26	14.7
TZ-3Y20A (ATZ)	TOSOH Corp., Japan	Y_2O_3 = 3.97 Al_2O_3 = 21.27 SiO_2 = 0.005	d_{50} = 0.27	13.6

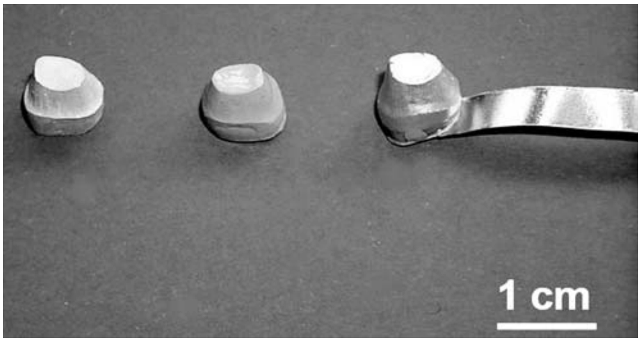

Fig. 1 Plaster stumps for dental crowns. From left to right original stump, stump coated with acrylate dispersion as intermediate layer, and stump prepared as deposition electrode with silver coating and copper ribbon

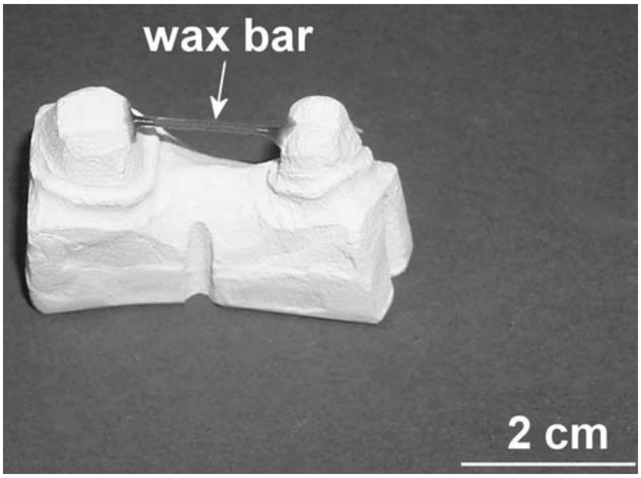

Fig. 2 Plaster stump of a four-unit dental bridge provided with a wax bar for electrophoretic shaping of bridge caps

20 min. During the experiments the current and the conductivity of the suspensions had been observed.

Because of the adhesion between the deposit and the electrode, the removal step of the compact from the plaster stump was the most critical step in the processing chain. For that reason, two possibilities for excluding this source of failure were investigated:

(1) For increasing the green strength and the flexibility of the deposit 2 wt.% of co-polymer (Butvar® B-98, Monsato) were added to the suspension. Previous to the binder addition measurements of the zeta potential vs. the binder content were carried out (ZetaProbe) with TZ-3Y suspensions containing either 1.5 wt.% benzoic acid or hydroxybenzoic acid. The aim of these measurements was to ensure that the binder addition would not affect the zeta potential negatively.

(2) The plaster stumps were coated with a thin layer of acrylate dispersion (Optapix AC 95, Zschimmer & Schwarz) previous to coating with conductive silver.

Immediately after the deposition process the deposits were removed carefully still in the wet state from the plaster stumps. Otherwise, drying of the deposits on the stumps always resulted in cracking. After drying the deposits were heat treated for removal of residual organic additives before sintering. For this treatment the bridges were embedded in fine-grained alumina powder to achieve a wicking effect of the powder bed for careful removing of the wax core out of the bridging part. Any liquid phase would destroy the sensitive deposit owing to the capillary forces. Pore size distributions were measured by mercury intrusion after drying. Optimal sintering conditions were estimated by dilatometry. Sintering of fully dense crowns and bridges was carried out at 1,450 °C for alumina toughened zirconia and at 1,500 °C for TZP for 1 h. The structure of the sintered dental components was investigated by SEM. The density was measured using the hydrostatic method. For achieving a certain amount of open porosity for dental glass infiltration the sintering temperatures were lowered to 1,050, 1,100, 1,150, 1,200, and 1,250 °C, respectively. The aim of these investigations was to reduce the shrinkage of the dental components during sintering. The porosity of the porous crown caps after sintering was measured by mercury intrusion. Afterwards, the dental components were cut and investigated by means of optical microscope.

Results and discussion

Both initial powders were positively charged in ethanol without addition of any dispersant. The influence of the various organic dispersants on the zeta potential of the TZ-3Y powder can be seen in Fig. 3. Since the diagrammed curves showed an almost identical course also for the TZ-3Y20A powder, only the curves for the TZ-3Y are shown here. Polyacrylic acid and polyethylene imine did not change the zeta potential of the zirconia powder in any way. In contrast, diethylamine decreased the initial value of the zeta potential and a combination of polyacrylic acid and diethylamine caused a drastic decrease and a change in the sign of the zeta potential. The powder became negatively charged even at very low amounts of these combined additives. The reason for this effect can be seen in the higher degree of dissociation of the polyacrylic acid

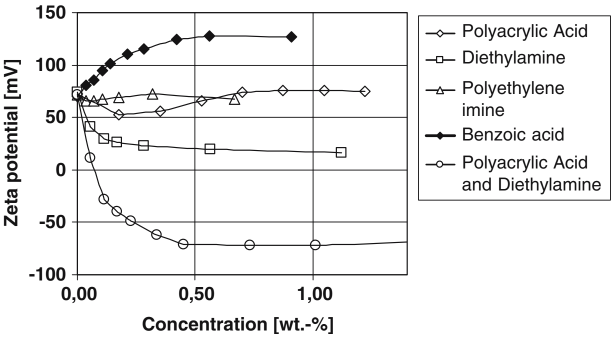

Fig. 3 Zeta potential versus concentration of organic dispersants for ethanolic suspensions of TZ-3Y (solid content 38 wt.%)

which is promoted in the presence of the alkaline diethylamine. Negatively charged dissociated acid molecules were adsorbed onto the powder particle surfaces, which provided them with a negative surface charge. Benzoic acid and hydroxybenzoic acid are known to be completely dissolvable in ethanol. Both dispersants provided the particle surfaces with a positive charge due to the adsorption of protons (Figs. 3 and 4). Both organic acids were chosen for the subsequent experiments on EPD of dental crowns and bridges. Stable suspensions with solid contents of 50–60 wt.% had been achieved with 1.5 wt.% of these dispersants.

Besides this charge increasing effect, benzoic acid such as hydroxybenzoic acid had a remarkable influence on the suspension stability and viscosity as shown in Fig. 5. Without the addition of any dispersing agent the viscosity of the ethanolic suspension increased drastically with higher solid contents, whereas the addition of 1.5 wt.% hydroxybenzoic acid decreased the dynamic viscosity and the suspensions showed an almost Newtonian behaviour.

The influence of temporary binder addition to the suspensions on the zeta potential is shown in Fig. 6.

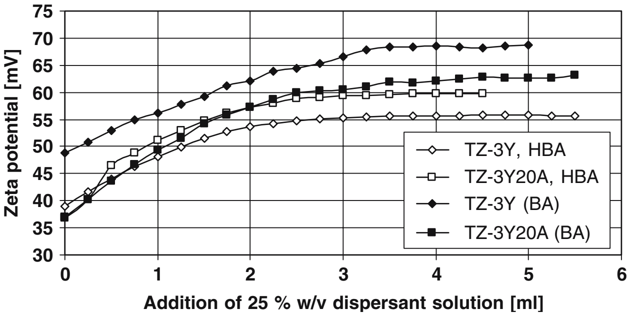

Fig. 4 Zeta potential vs. the concentration of benzoic acid (BA) and hydroxybenzoic acid (HBA) for ethanolic suspensions of the powders TZ-3Y and TZ-3Y20A (solid content 38 wt.%)

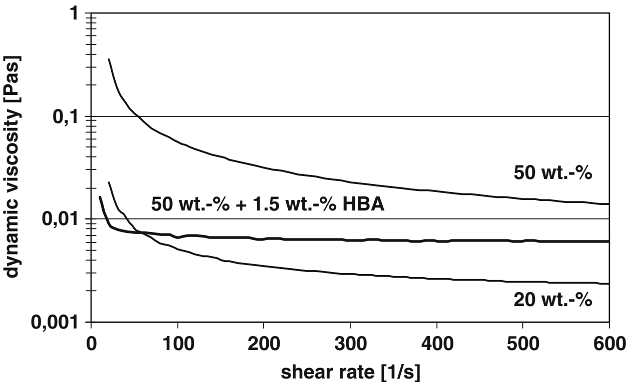

Fig. 5 Dynamic viscosity of ethanolic zirconia suspensions without dispersing agent and solid contents of 20 wt.% and 50 wt.%, respectively, such as of a suspension with a solid content of 50 wt.% containing 1.5 wt.% hydroxybenzoic acid (HBA)

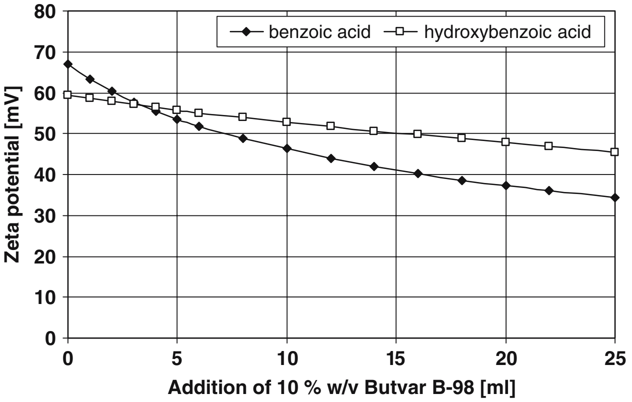

Fig. 6 Zeta potential of TZ-3Y and TZ-3Y20A suspensions in ethanol (260 mL initial sample volume) with 1.5 wt.% hydroxybenzoic acid and benzoic acid, respectively, versus the amount of temporary binder solution (Butvar® B-98)

With increasing binder concentration the positive zeta potential had been decreased. Hence, in smaller concentrations up to 2 wt.% this decrease did not show any negative effect on the stability and the deposition behaviour of the suspensions.

Since suspensions with hydroxybenzoic acid provided better deposition results in comparison to those containing benzoic acid, the following results are related without exception to suspensions with 1.5 wt.% hydroxybenzoic acid.

Figures 7 and 8 show the wall thickness of the deposited crown caps depending on both, the deposition voltage and the deposition time, whereas in the case of the ATZ powder TZ-3Y20A the deposition rate was higher than in the case of TZ-3Y. A reason for this behaviour can be seen in the slightly higher zeta potential of the ATZ powder. These investigations

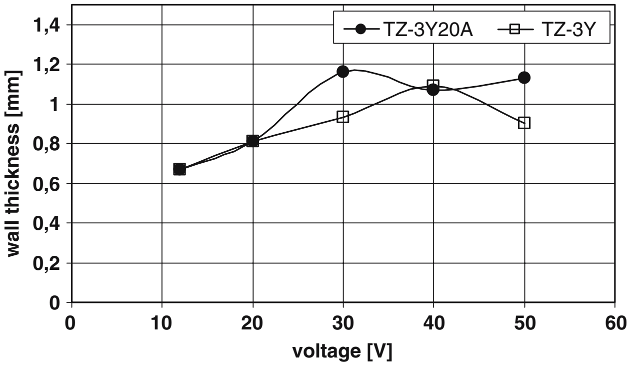

Fig. 7 Wall thickness of electrophoretically deposited crown caps in the green state versus the deposition voltage

were used for setting of optimal processing parameters for the deposition of dental crowns and bridges.

The handling and the removal of the crown caps and bridges could be improved remarkably by adding 2 wt.% of Butvar® B-98 to the suspension, because the deposits became more flexible. A crucial effect on the adhesion between deposition electrode and deposit was achieved by the intermediate layer of acrylate dispersion Optapix® AC 95. This polyermic material is known to be insoluble in ethanol, but it is soluble in water. Immediately after the EPD in the ethanolic suspension had been stopped, the plaster stump with the deposit was immersed into a mixture of ethanol and water (volume ratio 75/25) for approx. 30 s. The water content solved the acrylate layer, and after a short drying time of a few seconds the crown cap or the bridge cap could be lifted off the plaster stumps more easily, because the partially solved acrylate layer acted like a lubricant. The adhesion between the plaster stumps and the deposits was remarkably reduced. Cracks and deformations were prevented in this way.

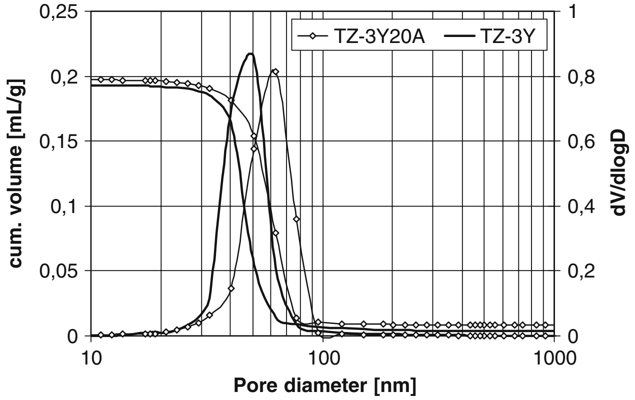

Fig. 9 Pore size distributions of electrophoretically deposited crown caps of TZ-3Y and TZ-3Y20A in the green state

The pore size distributions of the deposited powders TZ-3Y and TZ-3Y20A (Fig. 9) point to very homogeneous powder compacts with mean pore diameters of 50 nm and 60 nm, respectively, which were achieved by EPD of dental crown caps.

After sintering 99.7% of theoretical density were achieved for crown caps made of TZ-3Y and 98.2% of theoretical density for TZ-3Y20A. Sintered crowns and bridges are shown in Figs. 10 and 11. FESEM micrographs of both materials can be seen in Figs. 12 and 13, which confirm the almost pore-free microstructure.

In Fig. 14 the dilatometry curves of TZ-3Y and TZ-3Y20A are shown which were measured from pressed bars. Sintering starts at approx. 1,050 °C for both materials, and complete densification can be expected above 1,450 °C. The total shrinkage of zirconia is a little bit higher (23.7%) than that of the ATZ powder (21.9%). These relative high shrinkages are a critical fact and must be compensated by an oversize factor of

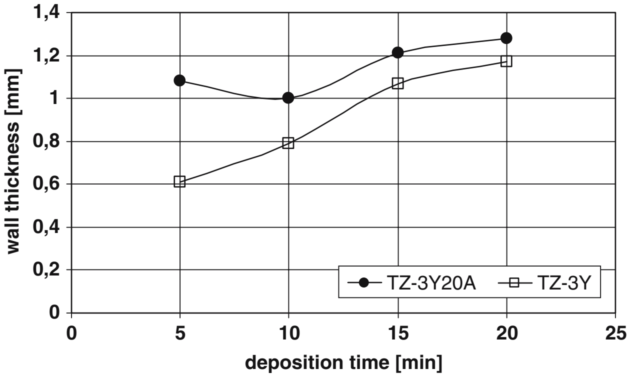

Fig. 8 Wall thickness of electrophoretically deposited crown caps in the green state versus deposition time

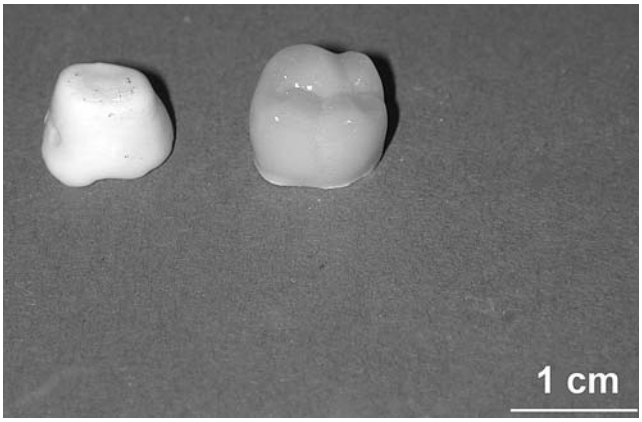

Fig. 10 Sintered dental crown cap without (left) and with (right) dental facing

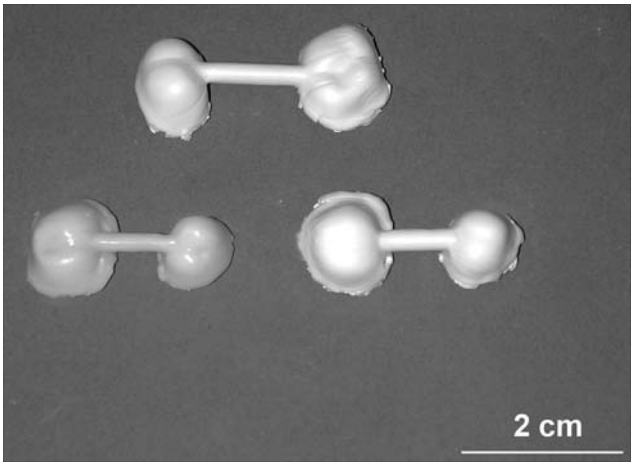

Fig. 11 Sintered three- and four-unit bridges without dental facing

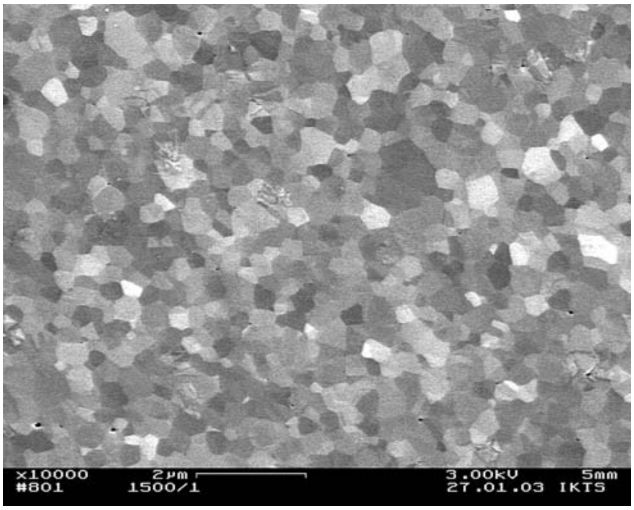

Fig. 12 FESEM micrograph of a sintered ZrO_2 crown cap

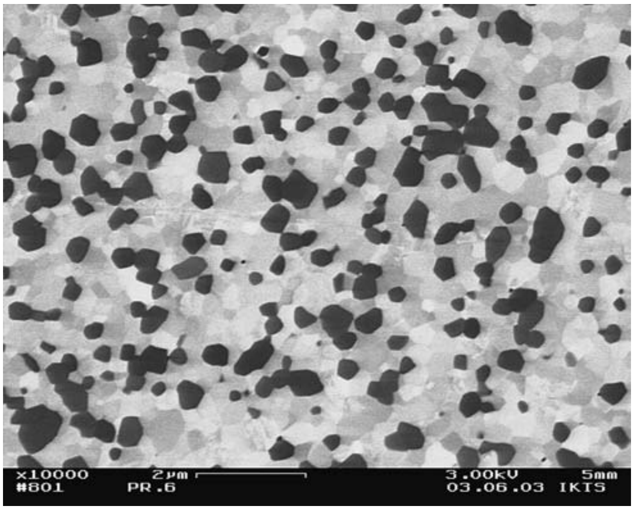

Fig. 13 FESEM micrograph of a sintered ATZ crown cap (dark phase belongs to alumina grains)

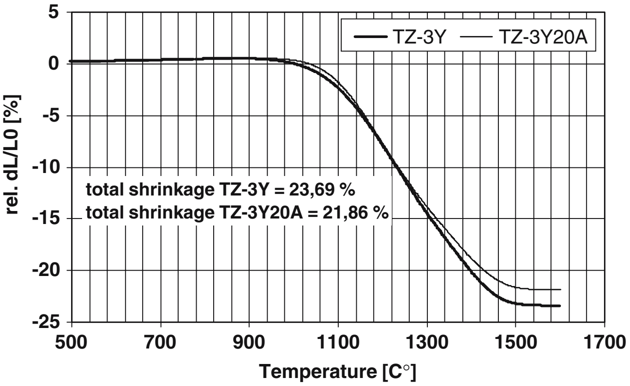

Fig. 14 Dilatometry curves of TZ-3Y and TZ-3Y20A sintered by exposure to air

the plaster stumps for manufacturing of very precise, dense crowns and bridges. For reducing the shrinkage it could be helpful to produce porous deposits at lower sintering temperatures, which can be infiltrated with dental glasses subsequently. However, it must be kept in mind that these porous, infiltrated structures cannot resist such high mechanical loads as dense ceramic structures do.

The results of the sintering of crown caps at different temperatures are given in Table 2. Main goal of this investigation was to achieve a high open porosity of the caps at sufficient mechanical stability for subsequent infiltration of dental glass. The right column of Table 2 contains the values of the linear shrinkage, which were estimated from the dilatometry measurements. Figure 13 shows a light microscopic image of a crown cap, sintered at 1,200 °C and infiltrated with dental glass afterwards. This crown cap showed shrinkage of only 7.5%, which can be compensated by an oversized plaster stump much easier than the total shrinkage of the dense materials (Fig. 15).

Table 2 Data of porous dental crowns made of TZ-3Y and TZ-3Y20A sintered at different temperatures

Temperature [°C]	Relative density [%]	Open porosity [%]	Linear shrinkage [%]
TZ-3Y			
1,050	47.4	50.8	0.79
1,100	51.0	47.2	2.35
1,150	57.8	40.4	4.48
1,200	64.2	33.2	7.75
1,250	73.4	25.2	10.9
TZ-3Y20A			
1,050	51.9	45.6	0.27
1,100	54.7	43.6	1.8
1,150	60.9	37.0	4.42
1,200	67.5	31.5	7.7
1,250	75.6	22.4	10.9

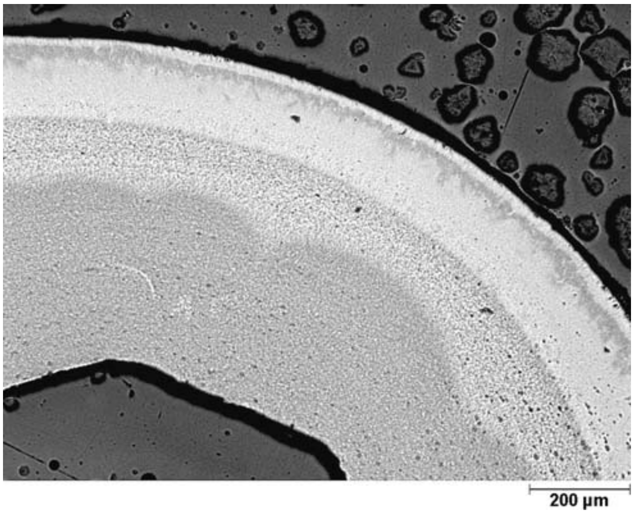

Fig. 15 Light microscopic image of a sintered crown cap (1,200 °C), subsequently infiltrated with dental glass

Conclusions

Dental crown caps such as three- and four-unit bridges made of zirconia and alumina toughened zirconia were developed by EPD from ethanolic suspensions for metal-free ceramic restoration. As electrodes for the EPD the plaster stumps of the teeth coated with conductive silver and a copper ribbon were used. In the case of the dental bridges the connecting bridge between both single crowns was realised by a wax bridge, which was thermally removed after the deposition.

The removal of the deposits from the relative complex shaped deposition electrodes was remarkably improved (1) by coating the plaster stumps with an acrylate dispersion which is insoluble in ethanol, but soluble in water, and dipping the deposits in a mixture of ethanol and water immediately after the deposition step for solving this intermediate layer, and (2) by using a temporary binder for increased flexibility of the deposits.

For reducing the total shrinkage of the dental parts during sintering, they can be sintered to a certain amount of open porosity and infiltrated with a dental glass afterwards.

The experiments have shown that EPD is a suitable wet-shaping technique not only for components with simple geometry, but also for complex shaped parts, which require a dense and defect-less structure.

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