Electrophoretic Deposition of Zirconia Nanoparticles

Stefan Frank¹, Carolina Mochales^{1*}, Martin Heimann¹, Felix Kochbeck¹, Rolf Zehbe², Claudia Fleck² and Wolf-Dieter Mueller¹

¹Dental School, Charité Universitätsmedizin Berlin, Germany

²Materials Engineering, Berlin Institute of Technology, Germany

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***Corresponding author:** Carolina Mochales, Dental School, Charité Universitätsmedizin Berlin, 14197 Berlin, Germany, Tel: +49-30-450-562756; Fax: +49-30-450-562923; E-mail: carolina.mochales-palau@charite.de

Abstract

Zirconia-based ceramics have gained considerable interest for several applications (e.g. solid electrolytes in fuel cells and in oxygen sensors, thermal barrier coatings and biomaterials for dental and orthopedic applications) due to their high mechanical strength, improved fracture toughness and easy affordability. Generally, one of the main disadvantages of ceramic materials is their brittleness, i.e. low fracture toughness. Electrophoretic deposition (EPD) has recently gained interest in the ceramics processing due to its wide versatility, allowing the fabrication of laminated and graded ceramics, fiber-reinforced ceramic matrix composites, coatings, and nanostructures. Moreover, EPD has been pointed out as an effective technique to obtain complicated 3D shape structures. This makes EPD a promising technique to obtain ceramic constructs for several applications like solid oxide fuel cells, thermal barrier coatings and biomaterials. In our research group, we have developed both a manual and automated EPD set-up to obtain tetragonal and cubic zirconia multilayered ceramic constructs. Multi layers of alternating tetragonal and cubic phases with a clearly defined interface were successfully obtained by an EPD layering process with submicron sized powders of Y-TZP with different mol percentages of yttrium oxide (3 % and 8 %). Finally, we investigated how to obtain 3D shape structures by EPD and we applied this technique to the dental materials field in order to obtain dental crowns.

Keywords: Electrophoretic deposition; Nanoparticles; Multi layered ceramics; Dental crowns

Introduction

Zirconia occurs in three crystal modifications at low-pressure conditions: monoclinic, tetragonal and cubic. The monoclinic phase is stable up to 1170°C, while the tetragonal phase is stable between 1170°C-2370°C, and the cubic one above 2370°C [1].

Doping of zirconia with dopants like CaO, MgO, CeO₂ and Y₂O₃ results in stabilization at room temperature of the tetragonal phase at dopant concentrations below ~8 mol% and in stabilization of the cubic phase at concentrations above ~8 mol%. The stabilization of the tetragonal phase results in a remarkable increase in mechanical toughness, whereas the stabilization of the cubic phase results in an increase of the ionic conductivity to values significantly higher than for other ceramics

[1,2]. This high ionic conductivity of the cubic zirconia makes it a very suitable material as electrolyte for solid oxide fuel cells (SOFCs). While tetragonal zirconia polycrystals (TZP) are being used in the dental and orthopedic field due to their relatively high toughness [3]. Moreover, the use of Yttria stabilized ceramics as thermal barrier coatings (TBCs) is of big importance [4].

Electrophoretic deposition is essentially a two-step process. In the first step, charged particles suspended in a liquid migrate towards an electrode under the effect of an electric field (electrophoresis); while in the second step, the particles deposit on the electrode forming a relatively dense and homogeneous compact or film. A post-EPD processing step is usually required, which includes a suitable heat-treatment (firing or sintering) in order to further densify the deposits and to eliminate porosity [5-7].

The interest in electrophoretic deposition (EPD) for nanomaterials and ceramics production has widely increased due to the versatility of this technique to effectively combine different materials in unique shapes and structures, like laminated and graded ceramics, fiber-reinforced ceramic matrix composites, coatings, and nanostructures [8-12]. Moreover, EPD has been pointed out as an effective technique to obtain complicated 3D shapes [13,14].

In our research work, we have started an EPD laboratory where we are able to produce several ceramic structures like multilayered specimens and 3D shape structures.

For instance, in order to optimize the properties of the final ceramic by combining the high mechanical toughness of the tetragonal phase of zirconia together with the high ionic conductivity of its cubic phase, we recently produced tetragonal and cubic zirconia multilayered specimens with a sharp and well inter connected interface by electrophoretic deposition of nano sized powders of Y-TZP with different mol percentages of yttrium oxide (3 % and 8 %) [15,16].

Finally, we also investigated the EPD of 3D shapes and we applied this technique to obtain ceramic dental crowns.

Methods

Samples preparation

EPD suspensions: The wide range of different zirconia multilayered samples as well as 3D shaped samples needed several varied suspensions. Two different Y_2O_3 -stabilized ZrO_2 powders (TZ-3Y with 3 mol% Y_2O_3 , and TZ-8Y with 8 mol% Y_2O_3) from Tosoh (Shunan, Japan) were used for the experimental investigations. According to the data given by the manufacturer the used powder contained 5.22wt % Y_2O_3 for TZ-3Y, 13.60wt % Y_2O_3 for TZ-8Y. The specific surface areas and crystallite sizes were 14.8 m²/g and 26 nm for TZ-3Y, 13.5 m²/g and 23 nm for TZ-8Y.

All solutions were prepared with ethanol (Merck KGaA, Darmstadt, Germany). In order to adjust the suspension's pH, either acetic acid (Carl Roth GmbH & Co. KG, Karlsruhe, Germany) or benzoic acid (Sigma Aldrich, St. Louis, USA) was added to the suspension. To produce the 3D shaped (i.e. dental crowns) a polymer was added to the TZ- 3Y solution to increase the flexibility of the final deposit. Prior to use, the suspensions were magnetically stirred for 45 minutes, followed by ultrasonic for at least 3 min, following for further 15 minutes of slow magnetic stirring.

EPD procedure: Different EPD set-ups were used to obtain the different samples showed in this paper. Figure 1 shows schemes of the three set-ups used: a manual (Figure 1a) and an automated (Figure 1b) set-up to produce tetragonal and cubic zirconia multilayered specimens, and a manual set-up to produce dental ceramic crowns (Figure 1c).

For the multilayered samples, aluminium electrodes were used in the manual set-up with a relative distance of 2.5 cm. The deposition area was around 25 mm – 30 mm by 10mm. The electrodes were fixed vertically in the manual set-up, while in the automated set-up they were fixed horizontally. For the automated set-up, the deposition area was 25 x 45 mm and the distance between electrodes was 3 cm. In the case of the dental crowns, a modification of the methods described in the literature

[17,18] was used. A plaster stump of a tooth was prepared by typical dentistry techniques and silver painting was applied directly on the plaster stump to create the deposition electrode. The counter electrode was made out of some metallic sheet (e.g. aluminium).

The EPD process of the multilayered samples was carried out at a constant DC voltage of 15 V for the TZ-3Y layers and of 10V for the TZ-8Y layers. TZ-3Y and TZ-8Y layers were deposited consecutively with a fixed deposition time of 30 min for each layer for the manual set-up (Figure 1a), whereas for the automated set-up it was between 1min and 5min. For the dental crowns, only one single layer of tetragonal zirconia (TZ-3Y) was deposited at either 15V other 30V in periods of time between 10min and 20min.

Final sintering: After drying and removal from the electrode, the deposited multilayered and 3D shaped single layer specimens (i.e. dental crowns) were sintered at 1450 °C for 3 h in a VITA Zyrcomat oven (Vita Zahnfabrik, Bad Saeckingen, Germany).

Samples characterization

The obtained zirconia specimens were investigated via optical microscopy using a regular microscope (Zeiss Axiophot, Carl Zeiss GmbH, Jena, Germany) and the InfiniteFocus® G4 microscope (IFM) (Alicona Imaging, Grambach/Graz, Austria).

The microstructure of the multilayered samples (cubic and tetragonal) and specifically the interface between the layers was analyzed using electron microscopy (SEM; FEI Quanta 600 FEG, FEI, Eindhoven, The Netherlands). To evaluate the yttria-distribution over the interface, energy dispersive X-ray (EDX) analysis was performed with an SEM S-2700 (High-Technologies Co., Japan) equipped with an EDX system (remX GmbH, Bruchsal, Germany) with a Si(Li) detector and a Moxtek AP 1.3 window (active area 10 mm²). The EDX-measurements were performed at 20 kV and a working distance between the detector and the sample of 17mm. Moreover, the fractured surface of a multilayered specimen subjected to four point bending test (4-PBT) was observed by SEM.

Figure 1: Schematic representation of the EPD set-ups used to produce: tetragonal and cubic zirconia multilayered ceramic specimens, both manually (a) and automatically (b), and tetragonal zirconia, dental crowns (c).

Figure 2: Tetragonal and cubic zirconia multilayered ceramic specimen manually produced by EPD (a), with an inset showing a SEM micrograph of the interface microstructure, which is magnified and showed together with the yttrium wt% content along the interface (b); SEM micrograph of a fractured surface after 4 point bending test (c).

Figure 3: Tetragonal and cubic zirconia multilayered ceramic specimens with different layers thickness produced by an automated EPD set-up (a), with a magnification showing the different microstructure between the tetragonal and the cubic layers (b).

Results and Discussion

Figure 2 shows a summary of the main characteristics of the tetragonal and cubic multilayered ceramic specimens obtained by using the manual set-up. Figure 2a shows one of the several obtained zirconia multilayered specimens. The used EPD process with constant deposition times for each layer resulted in several multilayered specimens with layers of different thicknesses between 12216 and 142 µm for the TZ-3Y, and between 383-139

µm for the TZ-8Y. The SEM observations (inset in Figure 1a, and Figure 2b) revealed a sharp and well inter connected interface between two different microstructures between layers. These well differentiated microstructures between layers were mainly tetragonal and cubic. EDX analysis (Figure 2b) confirmed a change in the corresponding yttrium, zirconium and oxygen amounts of the respective cubic and tetragonal layers. Indeed, this result is in accordance to the $\text{ZrO}_2\text{-Y}_2\text{O}_3$ equilibrium phase diagram as expected [19], as it is the yttrium which rules all the different

Figure 4: Overview of the EPD set-up, the plaster stump and the dental cap crowns obtained (a), with a transversal cut and a slice of the cap (b).

phase transformations in either tetragonal or cubic zirconia. Figure 2c shows the SEM inspection of the fractured surface of a multilayered specimen subjected to 4-PBT, which revealed significant crack deflection present on the interface between the TZ-3Y and TZ-8Y layers (red circles in Figure 2c). A more detailed discussion of the layers thickness evolution, microstructure and crack deflection in this EPD obtained tetragonal and cubic multilayered ceramic specimens can be found in a previous publication [15].

The production of much thinner layers was possible with the automated set-up, as can be seen in Figure 3. The automation of the EPD process facilitated the operating of the process and ensured a better reliability of the ceramic specimens. Moreover, the in-situ recording of the applied voltage, electric current and temperature during the whole EPD process was used to investigate the electric current evolution with deposition time for the several different layers obtained. More information about the automated set-up and the in-situ recording of the electrical parameters can be seen in a previous work of our group [16].

Figure 4 shows the ceramic dental crowns produced by EPD. An overview of the plaster stump used as deposition electrode and the obtained deposited caps can be seen in Figure 4a. To check the deposited layer in the cap shape we investigated a transversal cut and a slice of the cap (Figure 4b).

These results show that it is possible to obtain optimal ceramic deposits which present different hierarchical levels, i.e. different shape, layers, microstructures and dopant amount, which make these ceramic constructs promising candidates for several applications like solid oxide fuel cells, thermal barrier coatings and biomaterials.

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