

Aus dem Institut für Zahnärztliche Prothetik, Alterszahnmedizin und
Funktionslehre - Bereich zahnärztliche Werkstoffkunde und
Biomaterialforschung der Medizinischen Fakultät Charité –
Universitätsmedizin Berlin

Dissertation

**Electrophoretic Deposition (EPD) of Ceramics: A
potential technique to improve mechanical properties in
dental appliances**

Zur Erlangung des akademischen Grades
Doctor medicinae dentariae (Dr. med. dent.)

Vorgelegt der Medizinischen Fakultät Charité –
Universitätsmedizin Berlin

Von

Christine Fleckenstein
Aus Berlin

Gutachter/in: 1. Priv.-Doz. Dr. rer. nat. W.-D. Müller
 2. Prof. Dr. Dr. h.c. P. Fratzl
 3. Prof. Dr. P. Ginebra

Datum der Promotion: 23.06.2013

Contents

1	Introduction.....	5
1.1	Ceramics for dental applications: state of the art.....	6
1.1.1.	Dental ceramic restorations.....	7
1.1.2.	Ceramics processing.....	12
1.2.	Electrophoretic deposition.....	14
2	Objective of this Work.....	17
3	Materials and Methods.....	19
3.1.	Materials.....	19
3.2.	Electrophoretic deposition (EPD).....	20
3.3.	Set-up procedure development.....	21
3.4.	Production of samples.....	24
3.5.	Inspection of samples.....	25
3.6.	Preliminary mechanical tests.....	26
3.6.1.	Vickers hardness (microindentation).....	26
3.6.2.	Nanoindentation.....	28
4	Results.....	31
4.1.	Set-up.....	31
4.1.1.	Set-up geometry.....	31
4.1.2.	Suspension.....	32
4.1.3.	Electrode material and electrical parameters.....	34
4.1.3.A.	Platinum foil/plate.....	34
4.1.3.B.	Titanium foil/plate.....	35
4.1.3.C.	Aluminium foil/plate.....	35
4.1.3.D.	Carbon and gold- or gold sputtered PMMA.....	37
4.2.	Heating process.....	41
4.3.	Sample production.....	43
4.3.1.	Single-layered samples.....	43
4.3.2.	Multilayered samples.....	44
4.3.3.	Porous samples – first trials.....	46
4.3.4.	Samples for mechanical testing.....	49
4.4.	Sample inspection using scanning electron microscopy (SEM).....	52
4.4.1.	Alumina-zirconia layers.....	52

4.4.2. TZ-3Y/TZ-8Y layers.....	53
4.4.3. Porous samples – first trials.....	55
4.5. TZ-3Y/TZ-8Y multilayered sample preliminary mechanical testing.....	56
4.5.1. Vickers hardness.....	56
4.5.2. Nanoindentation.....	62
5 Discussion.....	63
6 Summary.....	79
7 Abbreviation Index.....	81
8 References.....	82

1 Introduction

This work is part of the DFG (Deutsche Forschungsgemeinschaft) Priority Program SPP 1420: “Biomimetic materials research: functionality by hierarchical structuring of materials”, “Hierarchy of microstructural features as the origin of fracture resistance in dentine and ceramic composites.” Whole teeth, specific sites in teeth as well as dental ceramic restoratives, which are used for permanent tooth reconstruction (crowns, bridges) have been studied in this project. Teeth and dental ceramics are compared, because they have to last under the same harsh intraoral conditions. An attempt is made to identify the structural features that contribute to toughness in human dentine, a natural hierarchical composite. Trials are performed to include these hierarchical structures in ceramic samples according to these findings

According to the aim of SPP 1420, and following literature research, the electrophoretic deposition (EPD) has proven to be a particularly suitable method of producing ceramic samples with features at different multiple length-scales. It is a versatile and cost-effective method, with which we are able to produce ceramic samples of differing thickness, structures and porosities [1, 2]. Interest has been growing in EPD in multiple applications particularly in the biomedical field, e.g. layered and functionally graded biomaterials, porous biomaterials, nanostructured coatings, hydroxyapatite and bioactive glass coatings for orthopaedic applications. The structure at the nano- and micro-scale, microscopic and macroscopic dimensions, stoichiometry and material properties can be easily controlled [3].

The aim of this work is to achieve an EPD ceramic fabrication set-up and to develop a production protocol for the EPD process in order to be able to control the parameters influencing the process and consequently the structure of the ceramic. The performance of different structural features in the ceramics, e.g. layering and porosity, by means of EPD is to be analysed. The knowledge acquired will be extended and applied to the fabrication of specific hierarchical structured ceramics within the framework of SPP 1420.

1.1. Ceramics for dental applications: state of the art

Ceramic materials gained importance in the field of biomedical applications, i.e. bioceramics, in the late 1960s. Bioceramics were initially considered as a possible successful alternative to metallic implants used in orthopaedics and dental medicine metals in order to increase their biocompatibility. During recent decades, the research and application of bioceramics in the field of biomaterials have experienced a tremendous evolution leading to different concepts as for instance tissue engineering where bioceramics function as “scaffolds” for cells to create new biological tissue [4, 5]. Generally, bioceramics are currently being used for different applications in the musculoskeletal system. They exhibit four possible tissue-implant reactions, which are detailed below with examples of typical medical ceramics [6, 7]:

- Nearly Inert: Minimal interaction with the host tissues is present and a non-adherent fibrous tissue covers the implant as the host tries to isolate itself from the foreign body. Fixation is achieved through pure mechanical interaction (morphological fixation). Examples: alumina and zirconia ceramics.
- Porous: Fixation is achieved through biological ingrowth of the host tissues into the implant pores (biological fixation). Examples: porous hydroxyapatite (HA) ceramics.
- Bioactive: Fixation results from chemical bonding between the implant and the host tissues (bioactive glasses, HA and bioactive glass-ceramics).
- Resorbable: The implant dissolves by chemical processes or is removed by cells. There is no fixation, only replacement of implant with biological tissues (α - and β -tricalcium phosphates, tetracalcium phosphate, dicalcium phosphate dihydrate and calcium phosphate glasses).

The choice between these types of bioceramics will depend on their final purpose. This work will be focused on the bioceramics used in dental restorations in which the main property that has to be fulfilled is the good mechanical response in terms of toughness. Nearly inert ceramics are the ceramics used in this application.

1.1.1. Dental ceramic restorations

Ceramic materials have been widely used for dental applications in the recent years, particularly in the restorative field, e.g. inlays, crowns, bridges or implants. This success is due to their excellent aesthetic properties and their ability to fulfil the patient's desire for invisible dental restorations. A lot of progress has been made in this field in the recent decades and the interest of producing metal-free ceramic restorations grew, particularly due to the desire for a tooth-like natural appearance of the restoration.

Different techniques exist to produce metal-ceramic or all-ceramic dental restorations. The first steps in the use of ceramic teeth in dentures were already taken in the 18th century [8]. The first fabrication procedure of the earliest versions of all ceramic crowns was in fact developed in 1887 [8]. The first all-ceramic crowns made of $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-K}_2\text{O}$ were produced in the 1960s [9]. These were called jacket-crowns. It became apparent very quickly, that these crowns were not stable enough to be applied in the posterior teeth region and not stable enough for long term use. This is the reason why efforts were made to cover a core metal with a ceramic material, because metals have been successfully used for dental applications for a long time. The ceramic and metal coefficient of thermal expansion could be approached and finally methods were developed to bond ceramics with metals. The first commercial systems were launched in the 1960s [8]. The application of ceramic materials in dentistry expanded in the early 1990s including endodontic posts, implants and implant abutments, orthodontic brackets, cores for crowns and fixed partial dentures [10].

The technique usually applied to produce dental restorations still involves the fusing of glass-ceramics to a metal core. A glass-ceramic, which originates mainly from the feldspar system, is bonded to the metal with the help of an intermediate layer, called opaquer [9]. The opaquer, an inorganic-inorganic composite containing glass, glass-ceramic and ceramic components, also covers the metal core to achieve a better aesthetic result. It creates a strong bond between the metal and the ceramic. After a heating process, which fuses the opaquer to the metal, the final glass-ceramic is applied on the opaquer. Finally, a second heating process is required. The firing temperature of the ceramic should be 150°C lower than the solidus temperature of the metal [8]. The

desire for all-ceramic restorations has not diminished despite the success of these metal-ceramic dental restorations.

The first technique used to produce all-ceramic restorations was the moulding technique. After a wax-up of the dental restoration, the model was invested and the wax fired out. The glass ceramic was pressed or cast into the resulting void at a temperature of between 1000°C and 1100°C. The core ceramic had to be veneered with another more translucent glass ceramic for aesthetic reasons. The high strength of the material made it suitable for application in posterior crowns [9]. In recent years, the CAD/CAM technique has gained considerable importance to produce all-ceramic restorations [11, 12]. This technique is based on the milling of very tough Al₂O₃ or ZrO₂. The surface structure of a tooth stump is scanned. Then the crown or bridge is virtually created using computer software (CAD). Afterwards, the crown, which was designed for the scanned tooth, is milled with a milling machine from a ceramic green body (CAM) [13]. These materials can also be veneered with glass ceramics in order to obtain better aesthetics. The veneering process has to be very well controlled, because developing stresses in the glass ceramic can lead to delamination [9].

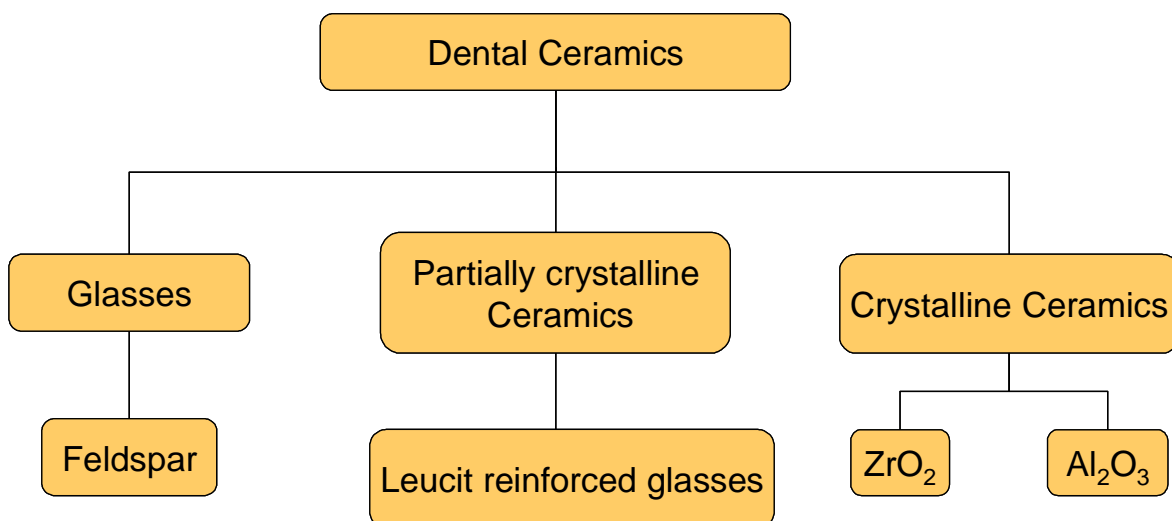


Fig. 1: Classification of dental ceramics

Zirconia is attracting particularly increasing interest in the application of dental restorations thanks to its excellent material properties. The material comprises better mechanical properties than any other material applied in dentistry, e.g. flexure strength between 800 MPa and 1000 MPa. The material has also been used for hip replacement prostheses thanks to its excellent mechanical properties [14].

Zirconia exhibits three phases: a monoclinic phase (stable up to 1170°C), a tetragonal phase (stable up to 2370°C) and a cubic phase (stable over 2370°C) [15]. The cubic and tetragonal phases are metastable. The three forms, which develop during the phase transformation, are reversible.

Thus, during the cooling process and during the sintering process, a phase transformation from the tetragonal to the monoclinic takes place. This is accompanied by an increase in volume (3-5%) [16].

Large internal stresses develop during cooling. Pure zirconia sintered above 1170°C may disintegrate by cracking during cooling [15].

This increase in volume has a negative influence, especially concerning the long-term stability of the material for medical application. With time, the material becomes brittle and breaks without significant deformation [16].

This is why stabilizers are added to zirconia in order to preserve the particles in the tetragonal phase during cooling, thereby inhibiting a spontaneous transformation to the monoclinic phase [16].

The stabilizers usually added are: CaO Calcium oxide, MgO Magnesium oxide, CeO₂ Cerium oxide and Y₂O₃ Yttrium oxide.

The stabilizers “freeze” the zirconia particles in the tetragonal phase at room temperature and inhibit transformation back to the monoclinic phase.

In the case of a propagating crack, a phase transformation from the tetragonal phase to the monoclinic phase is induced. This volume increase induces the development of compressive fields around the propagating crack [16]. This may impede the propagation of the crack. In addition to that, the transformation from tetragonal to monoclinic results in energy absorption that blunts the crack.

Zirconia can exhibit different modifications at room temperature due to the addition of the stabilizers mentioned above.

Fully stabilized zirconia (FSZ)

A fully cubic microstructure can be obtained. (Usually more than 8mol% of yttria or MgO needs to be added [17])

Partially stabilized zirconia (PSZ)

The major phase is cubic zirconia, with monoclinic and tetragonal zirconia precipitates as a minor phase at room temperature.

The monoclinic and tetragonal zirconia particles are evenly distributed at grain boundaries and inside the cubic matrix [17].

The more homogeneous the distribution of the monoclinic particles inside the cubic matrix, the better the mechanical strength [18].

The tetragonal particles can be in their pure form or stabilized either with Ca²⁺ (Ca-PSZ) or Mg²⁺ (Mg-PSZ)

Tetragonal zirconia polycrystal (TZP)

This modification only contains tetragonal particles at room temperature. Usually TZP materials contain 2-3 mol% of yttria. The tetragonal particles are usually metastable. Spontaneous t → m phase transformation can take place and so, in the case of a propagating crack, the propagation of the crack due to the volume increase accompanied with the t → m phase transformation can be suppressed [19]. The spontaneous phase transformation is dependent on the grain size, which is also attributed to the yttria content [17]. The fracture toughness apparently decreases with increasing yttria content [15]. Y-TZP ceramics have been successfully applied in dental restorations since the 1990s [10, 20-22]

Currently, Y-TZP is acquiring importance in the “new generation” of dental implants. Thanks to aesthetic reasons as well as thanks to their excellent biocompatibility, ceramic implants have been attracting increasing interest in recent years. The first ceramic implants were inserted 30- 40 years ago. But according to clinical studies, the use of zirconia implants is not yet recommendable for routine clinical application [23]. Titanium implants are still the first choice for dental implantation [23].

However, one disadvantage of Y-TZP ceramics is that they suffer from a phenomenon known as low temperature degradation. It takes place between room temperature and 400°C [15]. It is enhanced by the presence of water and water-vapour [24]. This degradation results in a large decrease in strength, toughness and density and is due to the tetragonal to monoclinic transformation which is accompanied by micro- and macrocracking. However, this transformation can be slowed by a decrease in the grain size and/or an increase in the stabilizer content [24].

Table 1 shows the main mechanical properties of 3 mol% TZP [17]

Table 1: mechanical properties of 3 mol% TZP

Density (gcm ⁻³)	>6
Porosity (%)	< 0,1
Bending strength (MPa)	900-1200
Compression strength (MPa)	2000
Young modulus (GPa)	210
Fracture toughness K _{ic} (MPa m ^{-1/2})	7-10
Thermal expansion coeff. (K ⁻¹)	11x10 ⁻⁶
Thermal conductivity (WmK ⁻¹)	2
Hardness (HV 0,1)	1200

Aside from the Y-TZP ceramics, glass-infiltrated zirconia-toughened alumina (ZTA) is also often used for dental purposes. The material can achieve excellent mechanical properties. In this case, an increase in volume, triggered by the t → m phase transformation, triggers the development of microcracks which then surround the transformed particles, thereby enhancing the toughness [14].

Another material used for dental application is partially stabilized zirconia (Mg-PSZ). Because of its poor mechanical properties it is rarely used currently. The material shows porosity and large grain size, which can induce wear. Besides, the fabrication process is complicated [14]. This is why interest is diminishing in this material for medical application.

1.1.2. Ceramics processing

The most common techniques to produce ceramics for medical applications are:

- pressing green bodies or white bodies
- HIP (hot isostatic pressing)
- WOL-CERAM®- system
- EPD

A) Pressing green bodies or white bodies

The white bodies are usually produced by cold isostatic pressing. A binder is added to zirconia powder agglomerates to make them usable for pressing. The zirconia blanks are then presintered. The dental restoration is designed by a computer software and is then milled from a zirconia blank using a computer aided milling machine. After the milling, a sintering process is required and a shrinkage of 20% during this process needs to be taken into account. The binder is eliminated during sintering. The restorations have to be veneered with a glass ceramic for aesthetic reasons [14].

The green bodies are not presintered and have a soft, chalk-like consistency. The powder water mixture is spray-dried and compacted in an automated press. The shrinkage of the milled ceramic body during sintering is huge. The green body exhibits only 60% of the final density [25].

B) HIP (hot isostatic pressing)

The hot isostatic pressing (HIP) takes place in a special oven under pressure (generally over 98 MPa [26]). The heating and sintering process takes place at the same time. This is why no binders need to be added [27]. The material is almost fully dense without any porous regions [26, 28]. Structures with homogeneously fine grain size and high purity can be obtained [22]. The HIP method reduces porosity, increases density and purity and leads to an increase in long-term service life [22]. This makes it applicable for production components resistant to very high loads. Since no sintering process is needed after milling, processing errors in the dental laboratory can be excluded. However, due to the high hardness of the block, the milling process is very time consuming and the diamond cutting tool wear is very high. These are undesirable

effects. Nevertheless, the fact that mistakes cannot be made in the dental lab in the production process of the ceramic core makes this method quite interesting. Possible failures occurring in the restoration can be attributed to the company producing the blocks and the resulting renewal costs of the dental restoration will have to be borne by the company and not by the dentist or dental technician.

Two of the most common zirconia based ceramics are In-Ceram Zirconia (IZ) and DC-Zirkon (DZ). IZ is a zirconia toughened alumina. DZ is a hot-pressed material doped with 5 wt% yttria. In comparison with IZ, DZ is stronger. It is shown that an increase in the crystalline content corresponds to an improvement in the mechanical properties [29].

C) WOL-CERAM®- system [30]

Wolceram is an alternative to the two techniques mentioned above. It is a combination of the dip coating technique and electrophoresis. In dentistry it is especially applied for the production of cores of dental all-ceramic crowns and bridges.

After the preparation of the tooth, an impression is taken from the tooth. The impression is filled with plaster by the dental technician. In this way, a model of the tooth is formed. The plaster tooth stump is dipped directly into a suspension containing ceramic particles. Figure 2 shows a) the WOL-CERAM® machine and b) a close-up of the dipping process [31, 32].

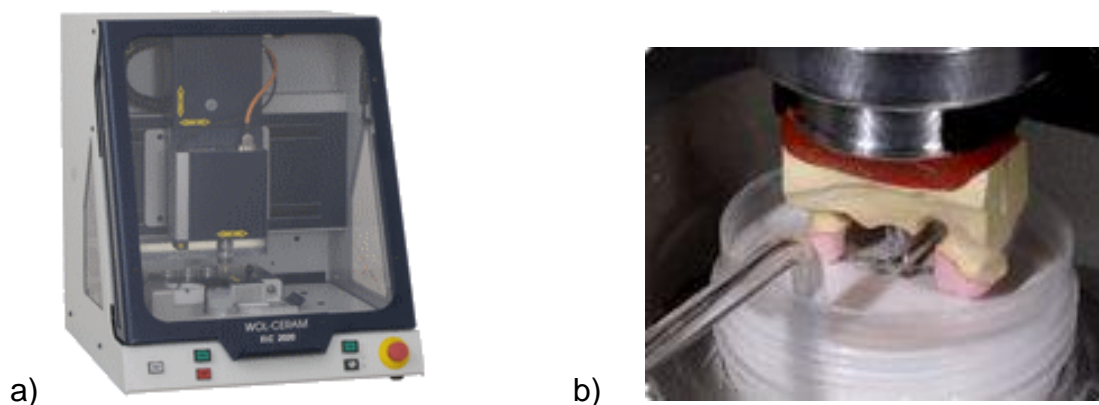


Fig. 2: WOL-CERAM® system a) machine [31], b) dipping process[32]

The plaster tooth stump serves directly as an electrode. The electrode is usually covered with a silver coating to aid conductivity. Then a tension is applied between the die and the suspension. The particles in the suspension are attracted to the die. After deposition the ceramic body needs to be further treated (e.g. dried, fitted, glass-infiltrated, veneered).

With this technique ceramic particles can be deposited as well as metal particles.

This technique is similar to the one applied in this work [30].

These industrial production processes can be very well controlled and the machined ceramic blocks are identical and accordingly very reliable. Processing errors in the dental laboratory can be excluded. Industrially fabricated ceramics are very successful in clinical applications. Nevertheless, sometimes problems (e.g. cracking, chipping) occur. The reasons for these phenomena are not entirely understood.

The basic idea of this work was to go back to the very beginning and choose one technique to produce ceramic bodies and to develop a new production protocol and thereby being able to understand every detail of the process and all the factors, which may influence the ceramic design.

1.2. Electrophoretic deposition (EPD)

EPD is a widely used ceramic processing technique for several industrial processes due to its cost-effectiveness and versatility. EPD has attracted interest in the biomedical field in recent years thanks to the possibility of producing unique microstructures and nanostructures as well as novel and complex material combinations of high interest for biomedical applications [33, 34].

Electrophoretic deposition (EPD) is a process based on the migration of particles that are suspended in a liquid medium under the influence of an electric field. Step 1 comprises the migration of charged particles suspended in a liquid towards an electrode. Step 2 is the particle deposition on another electrode forming a dense and homogenous layer [35]. After the deposition process, the sample needs to be further

treated, e.g. sintered. As mentioned above, this method has been attracting interest in recent years, because it can be used for a variety of applications, like bioactive coatings for biomedical implants and coatings for electronic components [33].

Generally, the EPD process can be applied to any product, which is available in a powder form with a particle size less than 30 μm (e.g. metals, polymers, ceramics, glasses and their composites) [33]. The method can be applied not only to many different materials, but also to many combinations of materials and for the production of coatings, different shapes, or complex three-dimensional and porous structures [3, 34]. Additionally, a great deal of work has been done in the application of EPD with hydroxyapatite (HA), particularly in bioactive coatings. HA has even been impregnated into porous metallic structures, such as meshes, as scaffolds for bone regeneration. Also scaffolds made entirely out of HA can be produced [3, 34].

Moreover, EPD has been successfully applied in the production of bioactive composite coatings (e.g. ceramic-ceramic coatings, polymer-ceramic coatings, layered and functionally graded coatings) [3, 34]. The idea of combining HA with, for example, a bioactive glass, is to improve the adhesion to the material to be coated, but at the same time to maintain bioactive behavior. Multi-layered coatings are obtained by moving the deposition electrode from one suspension to another, when the desired thickness of the first layer is obtained. By moving back and forth, layers are obtained [3, 34].

As mentioned above, the combination of EPD with different materials has proven to be successful. Fiber-reinforced ceramic matrix composites are well established in the production range of EPD. Moreover, efforts have been made to develop functionally graded Al_2O_3/ZrO_2 materials for ball heads and acetabular cup inserts thanks to their high fracture resistance [34, 36].

The use of Electrophoretic deposition from ceramic nanoparticles to the cores of dental crowns and bridges has been reported by Moritz *et al.* [37] and Oetzel & Clasen [13]. Precisely fitting cores can be produced, as the deposition process takes place directly on the plaster mould of the tooth stump. In order to control the pore size of the deposit, Oetzel and Clasen worked with a membrane [13]. While Oetzel and Clasen just produced the cores of dental crowns, Moritz *et al.* also produced the cores of dental bridges [37].

This is proof that with EDP even complicated or very delicate structures and forms can be produced.

The main application of EPD is still orthopedic implant bioactive coating with HA or bioactive glass. But a lot of research has been done in this field in recent years and new prospects, such as nanoceramic composite coatings with enhanced functionalities, e.g. drug delivery capability, or electrical conductivity have been identified [3, 34].

2 Objective of this Work

Zirconia-based ceramics are a very interesting material due to their excellent mechanical properties, e.g. mechanical strength, mechanical toughness, fracture toughness and biocompatibility. This is the reason why zirconia-based ceramics have gained considerable interest in dental and medical applications in recent years.

One big disadvantage with ceramics is their brittleness. Thus, when subjected to stress, they break without significant deformation (strain).

However, tetragonal zirconia particles (TZP) ceramics show a relatively high toughness due to a phenomenon popularly known as Transformation Toughening.

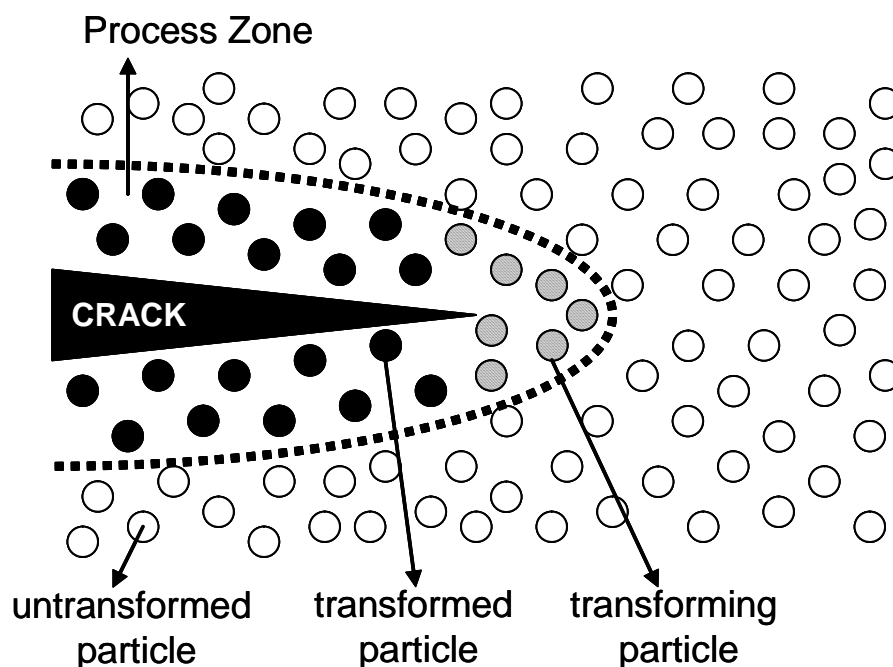


Fig. 3: Transformation Toughening

(Adapted from Butler EP, Transformation toughened zirconia ceramics. Mat Sci Tech 1985;1:417-432)

The transformation toughening mechanisms in TZP depend highly on the type and amount of doping used to stabilize the metastable t - ZrO_2 at low temperatures. Ytria (Y_2O_3) is the most used stabilizer in the dental and orthopaedic industry currently.

Despite the enormous success of ceramics for medical application, sometimes failures, e.g. spontaneous breaking or chipping, occur. As mentioned before, this work is part of a DFG project.

The objective of this part of the project is to work with a method (EPD) which enables us to produce our own ceramic samples in order to understand the multiple parameters influencing the production process of the ceramic and thus to be able to control the structure. This will allow us to gain a better understanding of the processes taking place and to comprehend why failures possibly occur.

It is important to mention that the set-up has been developed under the basic conditions of a dental laboratory. The aim was to develop a set-up, which is as simple as possible and which can be applied in any dental laboratory.

We produced samples with different compositions: Zirconia samples with different amounts of yttria (3 mol% and 8 mol%) as well as layered alumina-zirconia and TZ-3Y/TZ-8Y samples.

After the sample production, the structure of the samples was investigated with a scanning electron microscope (SEM) in order to ascertain the reliability of the process and our ability to reproduce the ceramic samples. Moreover, preliminary mechanical tests (Vickers indentation and nanoindentation) were performed.

3 Materials and Methods

3.1. Materials

The nanopowders used in order to produce the ceramic samples are the following yttria stabilized zirconia and alumina powders:

TZ-3Y (Tosoh)

TZ-8Y (Tosoh)

BMA15 alumina (Baikowski)

According to the manufacturer's data the crystallite size is 26 nm for the TZ-3Y, and 23 nm for the TZ-8Y powder. The alumina particles are bigger and range from 100 nm to 150 nm.

In order to be able to perform the electrophoretic deposition, a suspension needs to be prepared. Therefore the powders are suspended either in ethanol or distilled water.

The amount of powder is weighed with a precision scale supplied by Sartorius.

Acetic acid is also added to the suspension in order to adjust the pH and to deagglomerate the particles.

The deposition takes place on an aluminium foil electrode.

The deposition area is around 25 mm – 30 mm by 10 mm.

The applied tension (i.e. voltage) varies according to the powder and solvent concerned. The tension applied to the final electrode material is 15V for the TZ-3Y suspension, 10V for the TZ-8Y suspension and 30V for the alumina suspension.

In order to produce layered samples, first the deposition process is performed with the TZ-3Y suspension. Then the electrode with the single layer on it is dipped into the second, TZ-8Y or alumina, suspension and the tension is applied. The tension corresponds to the tension applied for single layers.

This process can be repeated as often as necessary, depending on the desired number of layers in the final sample.

The tension applied for the water-based suspension is 30V. This trial was only performed in preliminary tests on titanium and platinum electrodes.

The ethanol-based suspension is used to produce dense samples. Porous samples can be produced with the water-based suspension.

3.2. Electrophoretic Deposition (EPD)

Electrophoretic deposition is a general term for many industrial processes. It comprises the migration of particles suspended in a liquid medium in an electric field and the deposition on an electrode.

This process has been attracting interest in recent years, which is based on its cost-effectiveness and versatility. EPD is the technique of choice for ceramic coatings, which makes it applicable for bioactive coatings for biomedical implants, as well as for coatings for electronic devices [33].

It is a very simple method which comprises two steps. Step 1 is the migration of charged particles suspended in a liquid towards an electrode and step 2, the particle deposition on another electrode forming a dense and homogenous compact [35]. First, a cohesive particle layer is formed reproducing the electrode shape. Then, the solvent evaporation leads to particle packing and consequently to green body formation [35]. It has to be mentioned that step 2 of EPD is not completely understood up to now and still is a matter of discussion. Even electrohydrodynamic processes or electro-osmosis are considered to cause the movement of the suspension pushing the particles together [35].

The removal of the sample from the electrode appears to be an important and delicate step in the sample preparation procedure, because the deposited layers dry very easily on the electrode and crack quickly.

After the deposition and removal from the electrode, the layers have to be heated in an oven in order to be sintered.

The system of the EPD is a very sensitive one, because it is influenced by and dependent on many factors, like the set-up geometry, electrode material, suspensions, pH of the suspensions, the stirring of the suspension, deposition time, applied tension, the removal from the electrode and in the end the heating of the sample.

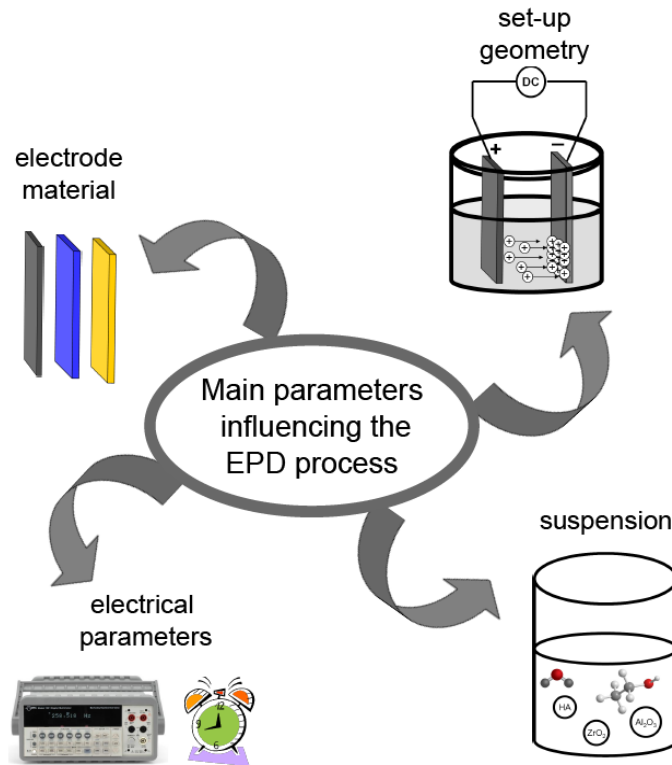


Fig. 4: Main parameters influencing the EPD process: electrode material, set-up geometry, electrical parameters and suspension

3.3. Set-up procedure development

Since the sample production process is very sensitive and complicated, it took several development stages to adjust the many different parameters and to achieve the final production protocol:

Table 2: Parameters to be adjusted for EPD process

Set-up geometry	Distance between electrodes, parallelism of electrodes
Electrode material	Platinum, titanium, sputtered plastic, aluminium foil
Adjustment of the Suspension (stirring and pH)	Water or ethanol based, Ultrasonic and magnetic stirring, Addition of acetic acid

Applied tension	Different for zirconia and alumina suspensions and for the different electrode materials
Deposition time	Depending on the desired thickness of the sample and age of suspension
Removal from electrode	Depending on the deposition electrode material
Heating process	Slow heating of the samples is necessary in order to avoid bending → 3 sintering programs

In order to produce reliable and reproducible ceramic samples, numerous different parameters have to be considered.

At first, a set-up design was developed in order to fix the electrodes in a retrievable position, and the electrode material was chosen.

Afterwards the suspension was adjusted. The third part comprised the ceramic sample treatment after deposition, e.g. removal from the electrode and heat treatment (pre-sintering and final sintering).

Table 2 and figure 5 show the various parameters that influence the deposition process. The number of parameters is very high. Moreover, the parameters influence each other. Changing one parameter entails changing others. If the electrode material or suspension is changed, the electrical parameters, e.g. time and tension, need to be adjusted accordingly.

By changing the powder particle size or the solvent, the suspension parameters need to be adjusted.

The fact that many parameters influence each other and depend upon each other made the production protocol development quite complicated and time consuming.

Two parameters stand apart from the others: the removal from the electrode and the heating process. These two parameters are independent of the EPD process. Nevertheless, it took some time to develop protocols to remove the samples from the electrode and especially to develop an appropriate sintering program. The heating process depends on many parameters, e.g. time, temperature, or heating rate.

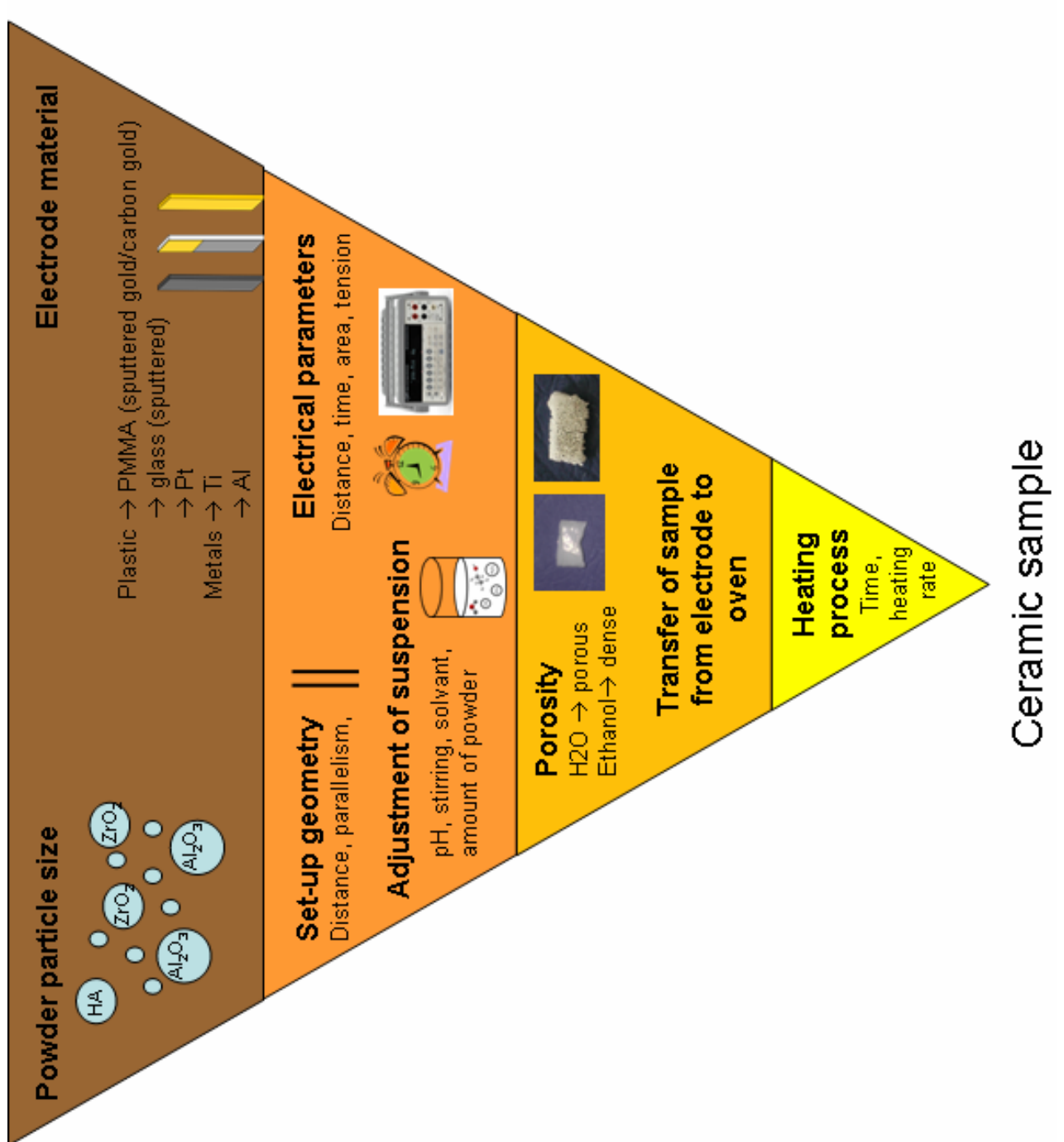


Fig. 5: Parameters for production of ceramic samples

3.4. Production of samples

Samples were produced from alumina suspensions and zirconia suspensions with different amounts of yttria doping (3 mol% and 8 mol%) on the final electrode material. For each suspension a production protocol was developed.

Additionally, trials with watery zirconia suspensions were performed and porous samples were produced.

Due to the growing interest in literature to layer ceramics in order to increase the material properties [38, 39], additionally, efforts were made to layer different ceramics. We produced layered samples with zirconia-zirconia layers with different yttria dopings or alumina-zirconia layers.

For layer production, first, one layer is produced with one suspension. After finishing the deposition of this layer, the electrodes are directly dipped into the next suspension. This is continued several times, depending on the desired number of layers.

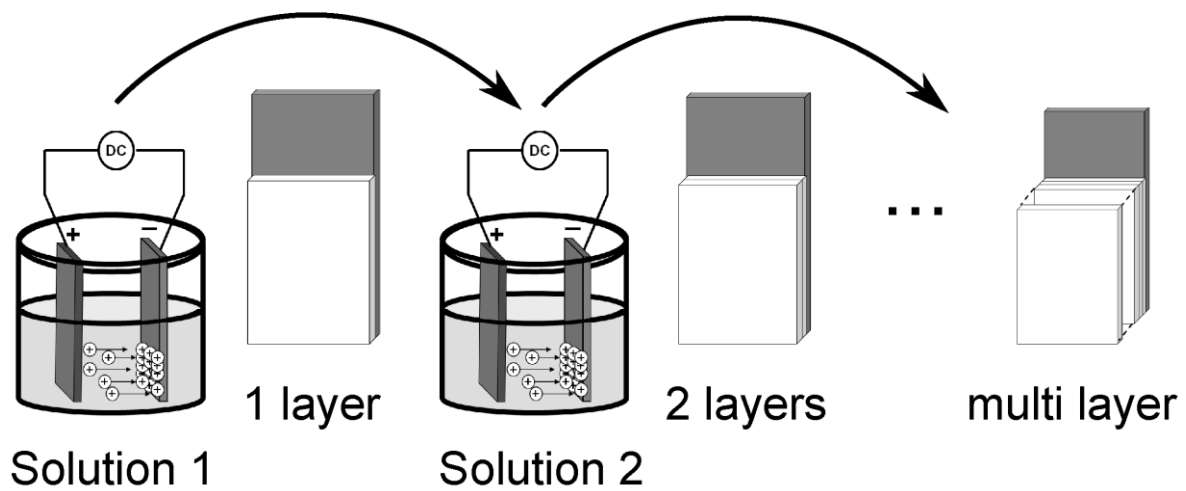


Fig. 6: Layer production

3.5. Inspection of samples

The ceramic samples were inspected with the aid of a scanning electron microscope (SEM).

The SEM scans the surface of samples with a very narrow electron beam. The atoms in the sample are activated. Signals, which give information about the sample's surface, are received.

With the SEM the surface and particularly the microstructure of the sample was analysed in detail. The samples were degreased with ethanol before inspection.

The SEM used is Maxim 4 from CamScan Electron Optics Ltd., Cambridgeshire, UK. It is also equipped with a backscattering detector, which was used.

For better pictures with a higher magnification and a better resolution, a SEM at the Max-Planck-Institute in Potsdam was used (SEM; FEI Quanta 600 FEG, FEI, Eindhoven, Netherlands).

a)



b)

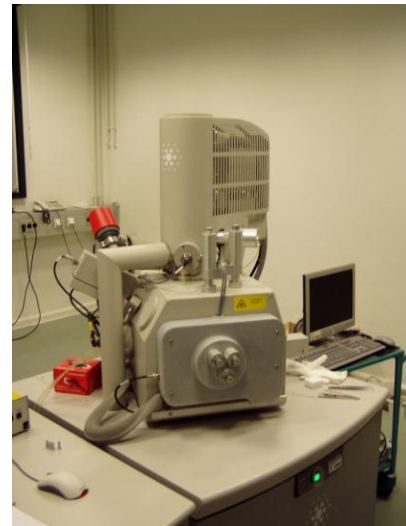


Fig. 7: a) Scanning electron microscope (Charité), b) SEM (Max-Planck-Institute)

3.6. Preliminary mechanical tests

3.6.1. Vickers Hardness (microindentation)

Before submitting the samples to microindentation testing, the samples need to be ground. Due to the manual handling before the sintering procedure, e.g. cutting the sample at the electrode edges, they do not exhibit a precise geometry, which is essential for the Vickers indentation test.

A grinding protocol was developed.

The first step is grinding with a very rough diamond grinding plate: MD Piano 120 produced by Struers. When a homogeneous and smooth surface is obtained, the sample is ground successively with 320, 800 (reduction of 100 µm per grinding step) and 1200, 2500, 4000 (reduction of 50 µm per grinding step) grinding papers WS flex 18C produced by Hermes. If necessary, the sample is then polished with 3µm and 1µm polishing spray: DP-spray P made by Struers. Each procedure of the polishing process lasts approximately 30 min.

After the grinding and polishing process, the samples are resintered in order to induce a transformation of the zirconia particles to a tetragonal phase again.

The final samples have an approximate width of 8.0 mm, thickness of 2.5 mm and length of 32 mm.

In order to determine the Vickers hardness, a diamond pyramid with a square shaped base is applied. The opening angle of the pyramid is 136°. This pyramid is pressed into the subject to be tested, here a ceramic sample, leaving an impression. The hardness can be determined by the quotient of the length of the diagonal of the impression and the applied force.

The machine used for indentation tests was Zwick 3212.

Before performing the indentation test, the samples were degreased with ethanol.

The applied load was 1 kg.

After the indentation was performed, the indents were optically measured with a microscope.

A Zeiss Axiophot microscope was used to optically measure the indents. DHS software was used to measure the photographs taken.

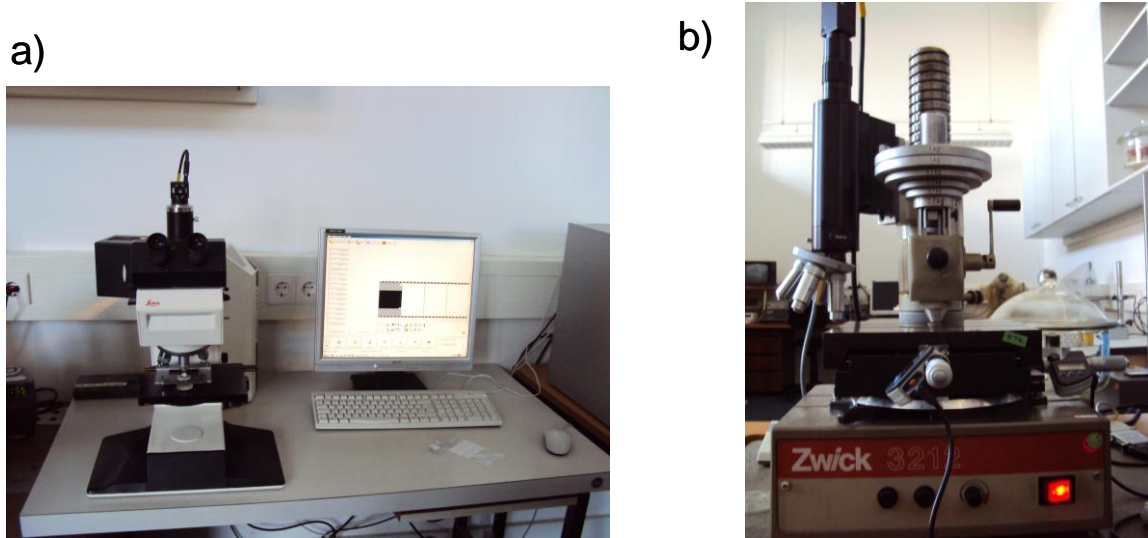


Fig. 8: a) Optical microscope and b) Zwick for indentation measurement

Afterwards the hardness can be calculated with the following formula:

$$HV = \frac{1,854 * F}{d^2} \quad \text{Eq. 1}$$

F: load (9,8N)

d: average diagonal

3.6.2. Nanoindentation

Nanoindentation is a powerful method of measuring near-surface mechanical properties of zirconia to much smaller length-scales than microindentation [40]. Usually a tetrahedral Berkovich diamond indenter tip is applied. The indentation machine performs several indentations in one area. Data is analyzed by the Oliver and Pharr method [41] providing information about the hardness H and the reduced Young's modulus E_r . The huge advantage of this method is the fact that very thin specimens, especially coatings, can be investigated and tested.

The scanning microindenter used to measure the samples was Ubi 1, Hysitron Inc., Minneapolis, USA. A tetrahedral Berkovich diamond indenter tip was used. The area of indentation was inspected with the optical microscope of the nanoindentation machine. The samples were loaded at a rate of $1000 \mu\text{N/s}$ with a maximum load of 10 mN . They were held under load for 15 seconds followed by a release time of 15 seconds. The data obtained was analyzed with the TriboScan software (Hysitron Inc., Minneapolis, USA, version 8.2.0.14) according to the Oliver and Pharr method [41].



Fig. 9: Nanoindentation machine and Berkovich indenter

Figure 10 shows the nanoindentation analysis by Oliver and Pharr.

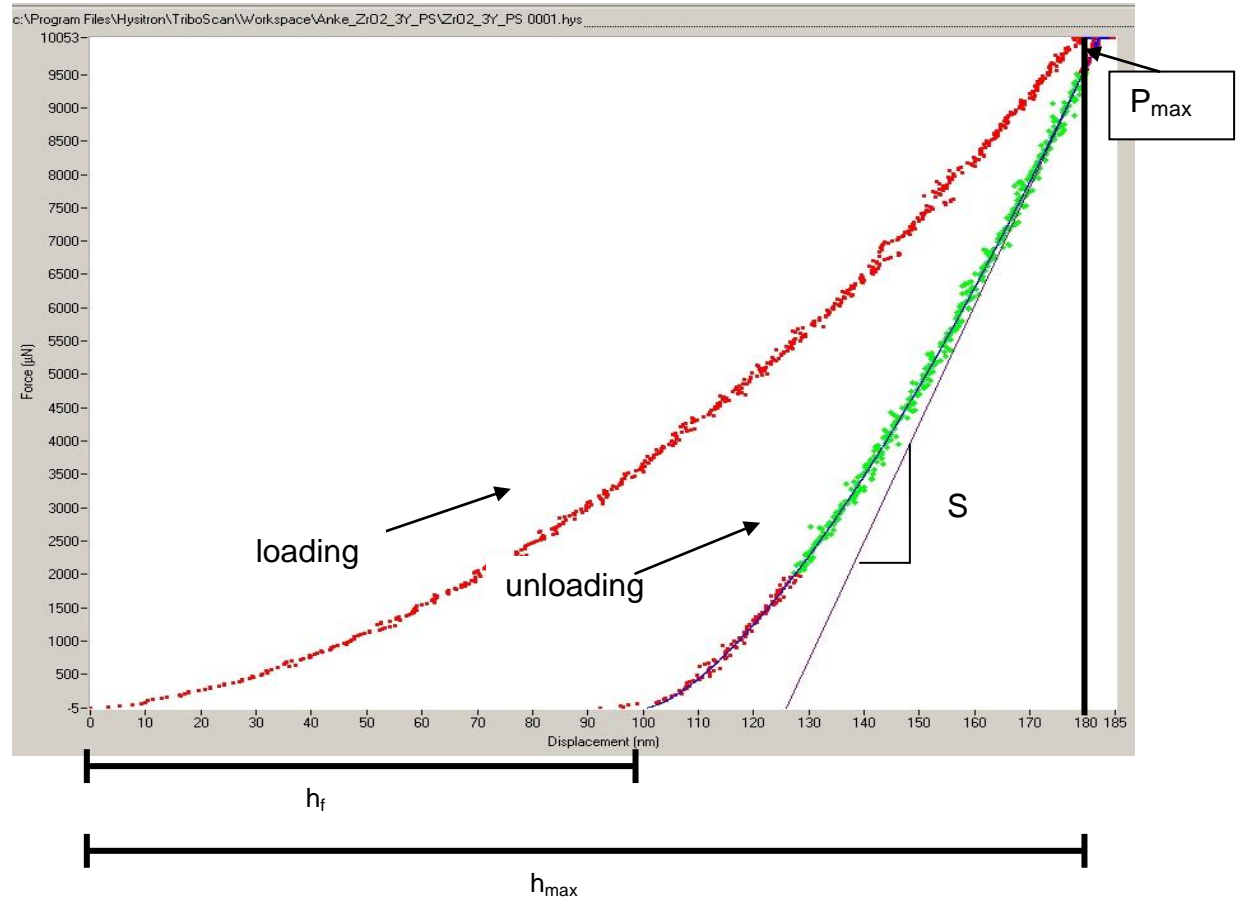


Fig. 10: Nanoindentation analysis by Oliver and Pharr

We can see the loading curve and the unloading curve.

A material displacement is assumed in this experiment.

P_{max} is the maximum load, before displacement sets in.

h_{max} is the indenter displacement at peak load and h_f is the final depth of the impression after unloading.

At peak load, load and displacement are P_{max} and h_{max} . Upon unloading, the elastic displacements are recovered. When the indenter is completely removed, the indent impression depth is h_f [41].

A tangent is fitted to the unloading curve to obtain S , which is the initial unloading stiffness. With the help of S , E_r can be calculated, assuming that the contact area of the indent is equal to the optically measured area of the hardness impression [41].

A is the projected area of the elastic contact [41].

H is the hardness.

$$H = \frac{P_{\max}}{A} \quad \text{Eq. 2}$$

$$E_r = \frac{\sqrt{\pi}}{2} \frac{S}{\sqrt{A}} \quad \text{Eq. 3}$$

4 Results

In this chapter the development of the subsequent production protocol for the electrophoretic deposition is described in detail.

Additionally, the results from the preliminary mechanical tests will be shown.

4.1. Set-up

4.1.1. Set-up geometry

A set-up was developed in order to create a fixed geometry and, consequently, to maintain a constant distance between the electrodes. The electrodes should not be positioned too far apart, in order to allow a dense particle packing, and parallel, in order to be able to obtain samples with homogeneous thickness. This is the reason why the following set-up was developed: a round plastic cover, which can be fixed to the cup containing the suspension. The inner diameter of the cover is 6.8 cm, the outer diameter is 7.9 cm. There are two slots in the centre of the cover where the electrodes (deposition electrode and counter electrode) are fixed. The distance between the electrodes is 2.5 cm.

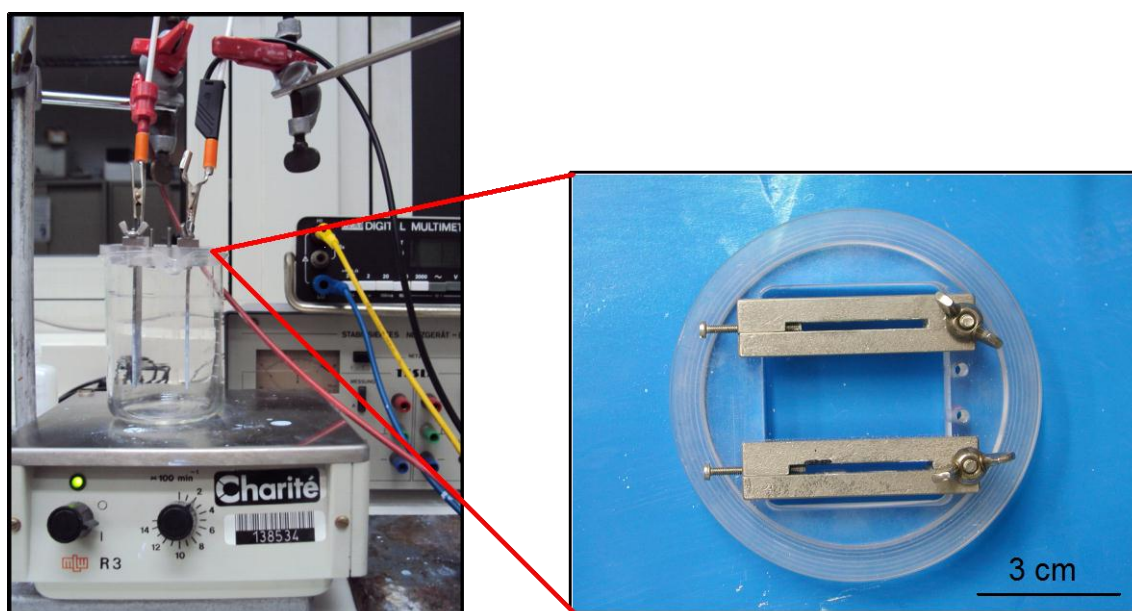


Fig. 11: EPD set-up

4.1.2. Suspension

As already mentioned in the materials and methods section, the suspensions are composed of powder, a solvent and a dispersant.

We chose powders with particles in the nanometer range, because layers with higher quality, for example less cracking, could be obtained [1, 42]. The composition of two types of suspension was determined: An ethanol-based suspension for the production of dense samples and a water-based suspension for the production of porous samples.

The amount of powder added to the zirconia suspensions is generally 80g of the zirconia powder (either TZ-3Y or TZ-8Y).

For the alumina suspensions, 10g of the alumina powder is weighed.

Because of the bigger crystallite size of the alumina particles, 100-150 nm, in comparison to 22 -26 nm in the case of the zirconia particles, it is more difficult to disperse and to deagglomerate them.

This is why the amount of powder in the alumina suspension is less than in the zirconia suspension.

Either 200 ml of 96% ethanol for the production of dense samples or distilled water for the production of porous samples is added after weighing the powder.

Moreover, it has to be mentioned that the TZ-8Y powder density is slightly lower than the TZ-3Y powder density.

The density of the powders was calculated by weighing the powders.

The obtained value for the density of the TZ-3Y powder is 1.263 g/cm³. The density for the TZ-8Y powder is 1.210 g/cm³.

This is the reason why the tension applied for the TZ-8Y is slightly lower.

144 µl of acetic acid is added to the suspension as the last component.

The suspensions were supposed to have a basic composition in order to limit the number of parameters, which can possibly influence the EPD process, so as to facilitate the process.

The acetic acid is needed to adjust the pH of the suspension and to deagglomerate the powder particles. A pH of 5 to 6 has proven to be ideal for the suspension.

Table 2: pH of suspensions

	TZ-3Y	TZ-8Y	Al₂O₃
pH	6.35	5.78	5.34

The suspension's pH level influences the surface charge (zeta potential) of the particles, which is a very important factor for the EPD process.

The particle surface charge should be high. With a higher surface charge, the density of the formed layer is higher, because the particles repulse each other and so occupy free positions [43].

However, if the surface charge is too high, the particles repulse each other in the suspension, which prevents agglomeration [1].

When the surface charge is low, the particles are consequently not densely packed. Besides, the inter-particle distances are greater and the deposited layer is porous and unstable [1].

As the final step, the suspension needs to be mixed manually with an ultrasonic nozzle. Afterwards it needs to be stirred with magnetic stirring for at least 3 days to be stabilized.

It became evident with time that the continuous magnetic stirring is a very important factor during use of the suspension. Particle segregation occurred regularly during initial trials: the sample was thicker at the bottom than at the top. This phenomenon was due to the vertical set-up and gravity. Moreover, the particles in the bottom part of the sample were not densely packed. The sample could not be removed from the electrode. It became evident that the particles were not deagglomerated sufficiently in the suspension. This problem was solved by the addition of more dispersant (e.g. acetic acid) and constant magnetic stirring for at least 3 days before suspension use.

4.1.3. Electrode material and electrical parameters

The following electrode materials were investigated:

- Platinum foil/plate
- Titanium foil/plate
- Aluminium foil/plate
- Carbon and gold- or gold-sputtered PMMA

The most promising materials, aluminium foil and sputtered PMMA, the decrease in the intensity (i.e. current) with time during the deposition procedure was studied.

4.1.3.A. Platinum foil/plate

Initial trials were performed with platinum foil as electrodes, because it is described in literature [44-46]. It is a highly conductive material.

The technical parameters applied in the initial trials were:

Table 4: Electrical parameters for the platinum electrode

EPD on Platinum electrode		
	Tension (V)	Time (min)
TZ-3Y + ethanol	60	30
TZ-3Y + water	30	30

4.1.3.B. Titanium foil/plate

Since platinum is a very expensive material, efforts were made to find a cheaper electrode material. Titanium was discovered to be suitable, because it is very cheap, but is suitably conductive.

Nevertheless, the tension that needs to be applied, is quite high. Additionally, the removal of the ceramic sample from the electrode was still problematic. Thus, the search for another, more conductive electrode material continued.

4.1.3.C. Aluminium foil/plate

Aluminium foil was discovered to be a suitable electrode material. It is highly conductive, so the applied tension is very low. It is highly energy efficient.

We use aluminium foil as an electrode, which is fixed with double-sided adhesive tape on a plastic carrier, in the final EPD procedure. A certain stiffness is essential for the electrode to prevent it from moving in the suspension with constant magnetic stirring during the deposition process. Besides, it is easier to fix it in the set-up. As counter electrode we use an aluminium plate.

The aluminium plate was not used as deposition electrode, as removal turned out to be more difficult than with aluminium foil.

The intensity/time graphs in figure 12 show a clear exponential decrease for the TZ-3Y and TZ-8Y suspension. This is expected for a correctly functioning EPD process. The graph showing the alumina suspension behaviour shows quite a linear curve. This is unusual. This may be attributed to the larger alumina powder particle size. The particles are not as easily moved and move slower. This may be attributed to the fact that the starting intensity is lower and the exponential decrease is not as significant as usual.

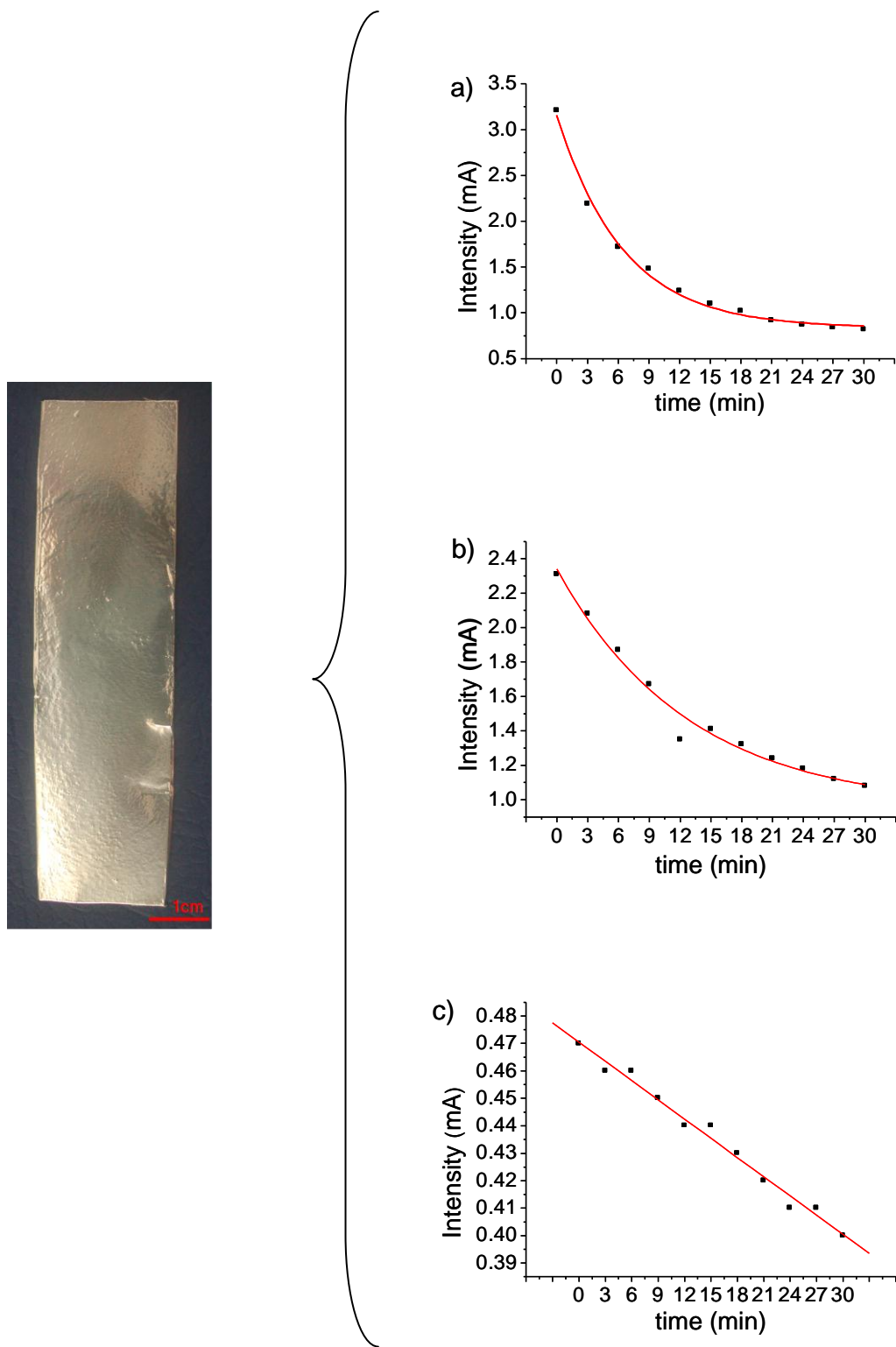


Fig. 12: Aluminium foil electrode intensity/time graphs: a) TZ-3Y, b) TZ-8Y, c) alumina deposited on aluminium foil electrode

4.1.3.D. Carbon and gold- or gold sputtered PMMA

Another electrode material tested was a plastic electrode sputtered with carbon and gold in the power supply contact area. Sputtering was required to make the plastic conductive. PMMA is widely used for medical applications nowadays, e.g. artificial dentures, bones, ophthalmic intraocular lenses. It comprises unique properties, like high hardness, high electrical resistance, high optical transparency [47].

An advantage of this electrode material are the low costs, because the PMMA foil, which is used, is very cheap. Additionally, the option exists to shape the electrode. This could be helpful for future trials, when we want to create defects in the samples.

Moreover, the material gives us the opportunity to use special PMMA foils, which induce specific particles into the layer by burning out during the sintering process.

But these are just ideas for future work.

The plastic electrodes were either sputtered with just gold (SCD 040, Balzers, Liechtenstein), or with carbon (MED 010 Turbo, Balzers, Liechtenstein), and gold in the contact area (i.e. carbon/gold sputtered electrode). The gold sputtering took place in a vacuum of 0,05 mbar and lasted for 2 min. For the carbon sputtering a commercial carbon wire was used. The sputtering took place in a vacuum of 10⁻⁵ mbar. Before sputtering, the large plastic plates were cut into small pieces (approximately 1.5 cm x 5 cm) and dried well. The electrodes were fixed in the EPD set-up after sputtering.

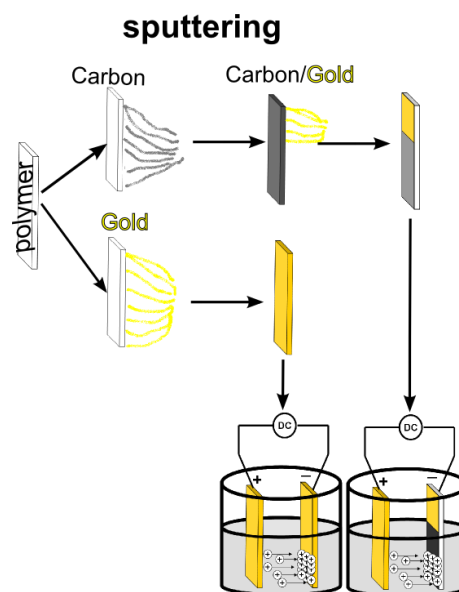


Fig. 13: Sputtering and EPD on PMMA electrodes

The EPD process was carried out with the TZ-3Y and alumina suspension with both the gold and the carbon/gold sputtered electrode as the deposition electrode. The counter electrode remained a gold sputtered electrode.

The current applied was 80V for the ZrO_2 suspension and 120V for the Al_2O_3 suspension. The deposition time was 30 min in each trial.

Nice homogeneous layers with both deposition electrodes (gold- and carbon/gold sputtered) were obtained with both suspensions.

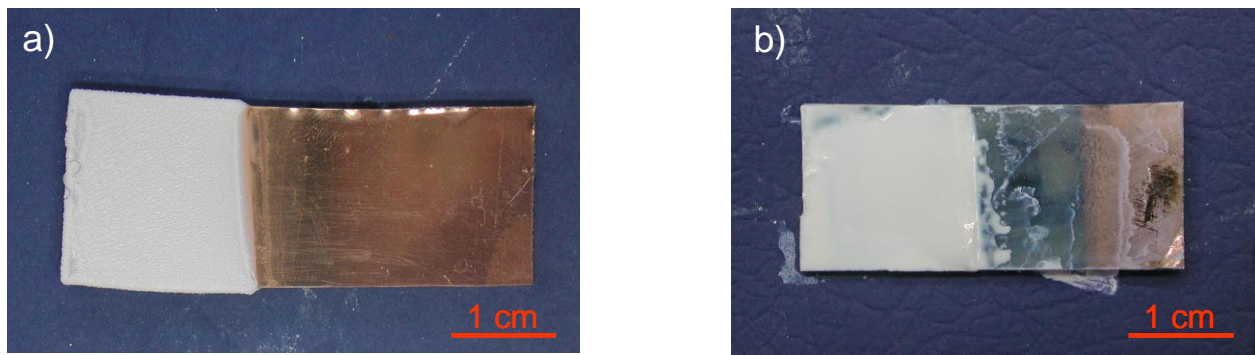


Fig. 14: TZ-3Y deposited on a) gold and b) on carbon/gold sputtered electrode

It can be seen from the layers produced, that the deposition on gold is better than that on the carbon coating, which can be explained by the higher conductivity of gold. This fact also explains why it was not possible to obtain a layer on an electrode, which was just sputtered with carbon without gold contact. However, the carbon/gold sputtered layer is not as conductive as the gold layer.

The starting intensity for the gold electrode is higher than that of the gold/graphite electrode. This is related to the gold electrode's higher conductivity. Moreover, the ZrO_2 slurry has a higher starting intensity than the other suspension. The intensity curves show an exponential decrease tendency as expected for an EPD process.

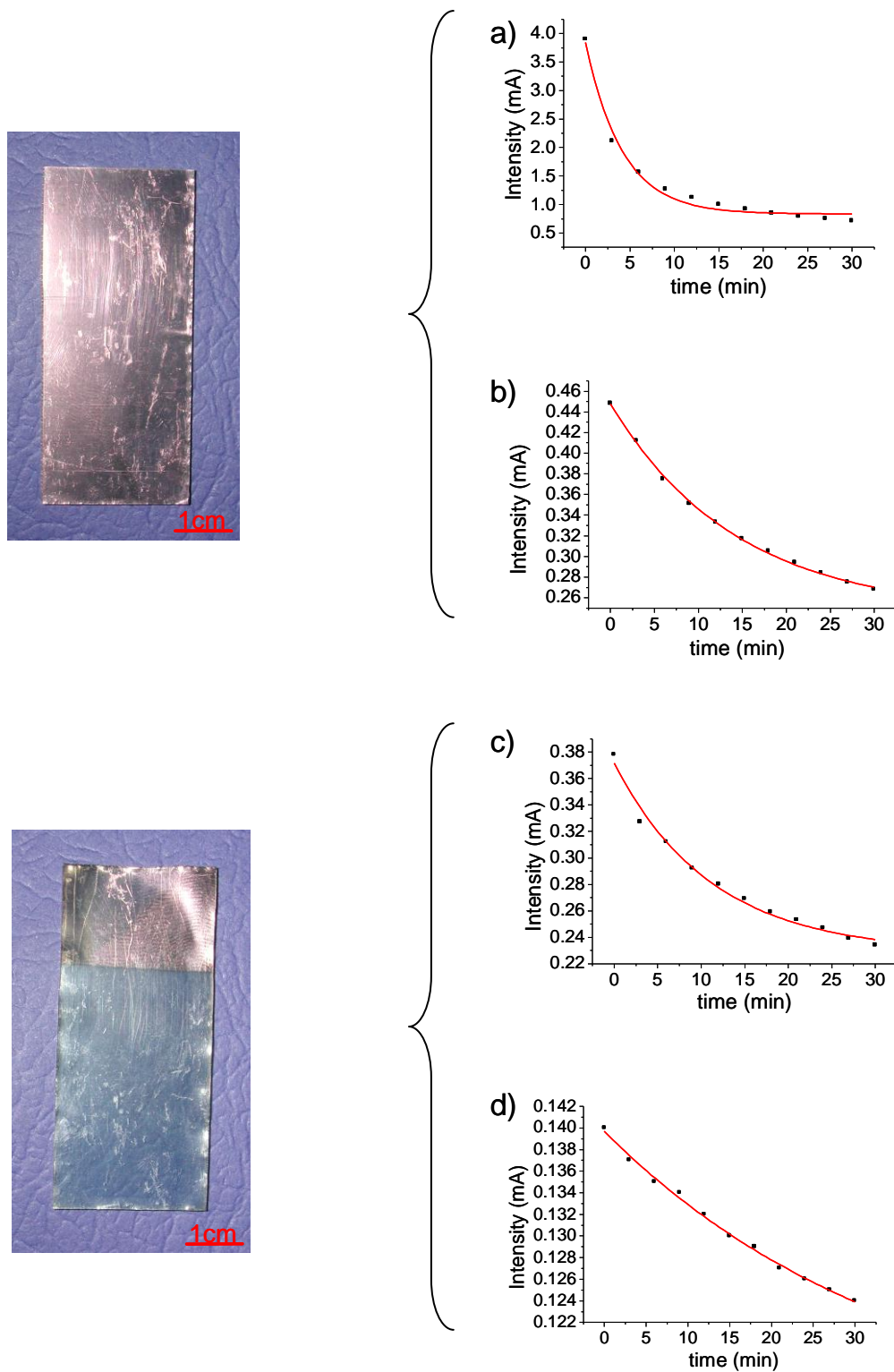


Fig. 15: Sputtered PMMA electrode intensity/time graphs: a) TZ-3Y deposited on gold sputtered electrode, b) alumina deposited on gold sputtered electrode, c) TZ-3Y deposited on carbon/gold sputtered electrode d) alumina deposited on carbon/gold sputtered electrode

In addition to the electrode material, the electrical parameters needed to be adjusted. These parameters were different for each electrode material and suspension. Table 5 gives a summary of the parameters and the corresponding electrode materials.

First of all the tension was adjusted. The tension is different for each electrode material. In general it can be stated that the lower the conductivity of the electrode material, the higher the tension applied needs to be. Moreover, it can be said, that generally the tension needs to be increased with the increasing size of the particles in the powder.

The deposition time depends on the desired final thickness of the sample. The longer the deposition time, the thicker the sample.

Table 5: Summary of the electrical parameters

Electrode material (deposition)	Electrode material (counter)	suspension	Tension (V)	Time (min)
Pt	Pt	TZ-3Y-ethanol	60	30-60
		TZ-3Y-water	30	30-60
Ti	Ti	TZ-3Y-ethanol	80	30-60
		TZ-8Y-ethanol	80	30-60
		Al ₂ O ₃ -ethanol	120	30-60
		TZ-3Y- water	30	30-60
Gold sputtered plastic	Gold sputtered plastic	TZ-3Y-ethanol	80	30-60
		Al ₂ O ₃ -ethanol	120	30-60
Carbon/gold sputtered plastic	Gold sputtered plastic	TZ-3Y-ethanol	80	30-60
		Al ₂ O ₃ -ethanol	120	30-60
Aluminium foil	Aluminium plate	TZ-3Y-ethanol	15	30-60
		TZ-8Y	10	30-60

4.2. Heating process

After sample removal from the aluminium foil electrode, they are put into the first oven: Vita Inceramat II. The samples are sintered at up to 500°C with program 1. Then the samples are heated up to 1000°C with program 2.

After that they are sintered at up to 1450°C with the Vita Zyrcomat.

The detailed heating processes can be seen in figure 16.

Three sintering programs are necessary in order to allow a very slow heating process, which is necessary to avoid the samples' bending during heating.

The importance of a slow heating and cooling process is also described in literature [48, 49]. Otherwise, stresses develop particularly due to the zirconia phase transformation, which lead to sample deformation or bending.

We used a customized sintering program in the Vita Zyrcomat with a quick heating rate (16.78 °C/min) in the initial trials.

The samples were bending a lot and were deformed. Even after programming another heating program in the Vita Zyrcomat with a slower heating rate (3.14°C/min) the samples were still bending slightly. Apparently, the heating rate was still too fast. This is the reason why a second oven was introduced in the heating process, the Vita Inceramat. This allowed us to create a heating process with a very slow heating rate.

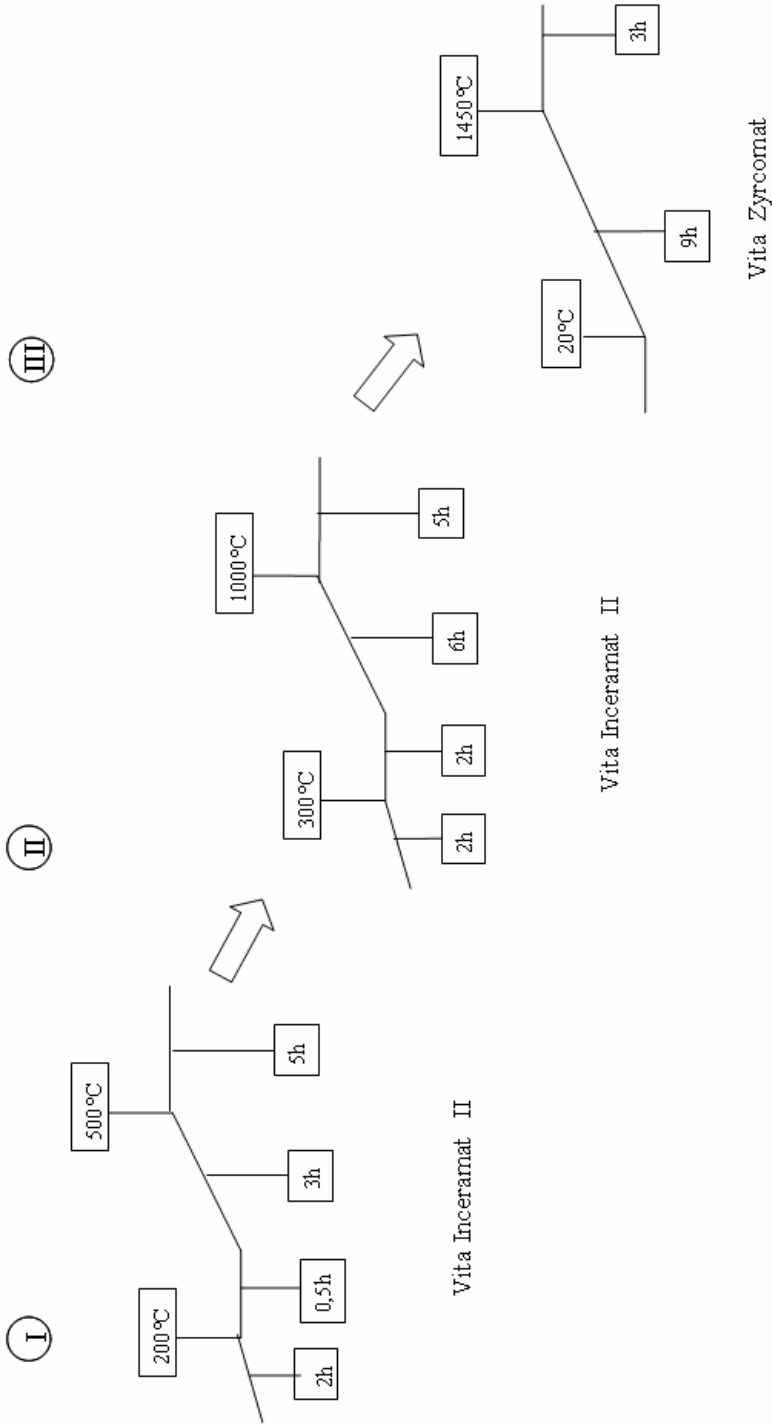


Fig. 16: Heating processes

4.3. Sample production

We created production protocols for single TZ-3Y or TZ-8Y layers, single alumina layers, single porous TZ-3Y layers, TZ-3Y/TZ-8Y layers and TZ-3Y/alumina layers.

4.3.1. Single-layered samples

The EPD process is performed with the aluminium foil electrodes mentioned above.

In order to perform the EPD process, the electrodes are fixed in the set-up. Then the set-up is fixed to the cup containing the suspension. This way the electrodes are dipped into the suspension. Then the tension is applied. The tensions applied for the respective electrode material are shown in table 6.

The tension for the TZ-8Y is lower than the applied tension for the TZ-3Y. This may be due to the higher density of the TZ-8Y powder.

The thickness of the sample is dependent upon the length of the deposition period. The longer the deposition period, the thicker the sample. The thickness of the deposit decreases with the frequency of use of the suspension with constant time.

This can be explained by the loss of powder in the suspension during previous deposition processes. Thus, the more often the suspension was used, the more the deposition time needs to be extended.

Table 6: Electrical parameters for the deposition of single layers

EPD single layers				
	Al foil		Ti	
	Tension (V)	Time (min)	Tension (V)	Time (min)
TZ-3Y	15	30-60	80	30-60
TZ-8Y	10	30-60		
TZ-3Y (porous)			30	30-60
Al₂O₃	30		120	30-60

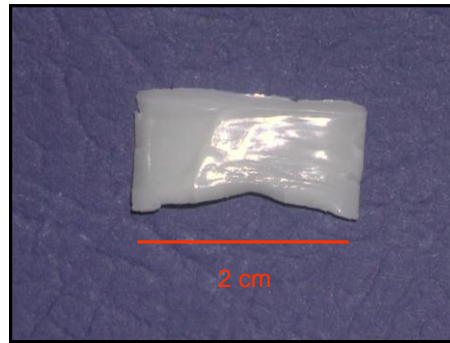


Fig. 17: Dense TZ-3Y single layer (deposited on platinum electrode)

4.3.2. Multilayered samples

After production protocol development for single zirconia and alumina samples, we also developed a protocol for layered samples. Two different series of layered samples were produced:

- TZ-3Y/alumina layers
- Zirconia-zirconia layers with different amount of yttria, 3 mol% or 8 mol%

Table 7: Electrical parameters for TZ-3Y/alumina layers

EPD of TZ-3Y/alumina layers on titanium electrode		
	Tension (V)	Time (min)
TZ-3Y	80	10
Al_2O_3	120	15
TZ-3Y	80	10
Al_2O_3	120	30
TZ-3Y	80	20

Table 8: Electrical parameters for the deposition of TZ-3Y/TZ-8Y layers

EPD of TZ-3Y/TZ-8Y layers on aluminium foil		
	Tension (V)	Time (min)
TZ-3Y	15	15
TZ-8Y	10	15
TZ-3Y	15	15
TZ-8Y	10	15
TZ-3Y	15	15
TZ-8Y	10	15
TZ-3Y	15	15
TZ-8Y	10	15
TZ-3Y	15	15

The layers are produced by a deposition process with one suspension. Afterwards, this single layer is dipped into the next suspension and a second deposition process is performed. By changing back and forth, a layered ceramic sample can be produced. This process can be repeated as often as necessary, according to the desired number of layers.

As can be seen in the tables, the deposition period needs to be extended with increasing numbers of layers.

Trials were performed initially by increasing the tension with increasing numbers of layers to compensate for the isolating layer on the electrode and the decreasing conductivity. We discovered that by increasing the tension, the layer that was produced before was destroyed. It is probable that the moving particles in the EPD process contained too much energy and pushed the particles in the existing layers aside and so removed the layer.

By prolonging of the deposition period for each layer, the increasing distance from the electrode can be compensated for without damaging the layer underneath. With increasing sample thickness, the deposition period has to be increased successively in order to obtain similar thicknesses of the intermediate layers. This fact has been described in literature as well [39].

Zhang derived an equation for the EPD kinetics for the deposited mass as a function of deposition time [50]:

$$m(t) = m_0 \left(1 - e^{-\frac{\mu \cdot E}{d} t} \right) \quad \text{Eq. 4}$$

m_0 = initial mass of particles in suspension

d = distance between electrodes

E = intensity of electric field

μ = electrophoretic mobility of particles

t = deposition period

The deposition process performed still needs to be analysed according to this equation. The precise time prolongation for each intermediate layer is a matter for further investigation.

4.3.3. Porous samples – first trials

Porous samples can be produced from watery suspensions. The pores develop due to the evaporation of H₂ and O₂ during the deposition process. This leads to bubble development. The evaporation of H₂ and O₂ of course inhibits particle agglomeration and homogeneous layer formation. The particles are removed due to the ascending bubbles.

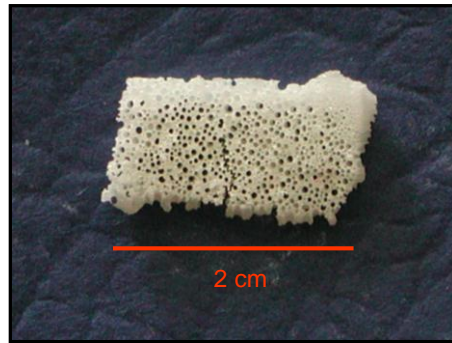


Fig. 18: Porous TZ-3Y single layer (deposited on platinum electrode)

It is a practical way to produce porous structures, but one disadvantage is the fact that the distribution of the pores and the pore size cannot be controlled.

According to Moritz *et al.*, the pore size and distribution can be controlled and influenced by the addition of electrolytes and other additives to the suspension, the solids content of the suspension, or the electrical parameters [44].

With increasing tension, the pore size increases. Additionally, Moritz *et al.* control the pore size and distribution by adding a platinum gauze to the EPD set-up and placing it in front of the deposition electrode [44].

The electrical parameters for the production of porous samples are a tension of 30V for a minimum deposition time of 15 min.

For this reason, it was a big step forward when we discovered that porous deposits can also be obtained by covering the deposition electrode with a wax mixed with metal particles.

Titanium powder was mixed with molten wax. Then the titanium electrode was covered with the liquid wax and then cooled down. The deposition process was performed. Due to the inhomogeneous distribution of the titanium particles in the wax, a porous layer was obtained. But there was no control of the distribution of the pores.

Still, this method will be subject of further investigation. It is a way to produce porous layers. Maybe it is possible to control the distribution of the metal particles in the wax and thereby to control the porosity of the sample.

The wax-electrode seems to open and offer new prospects in this field.

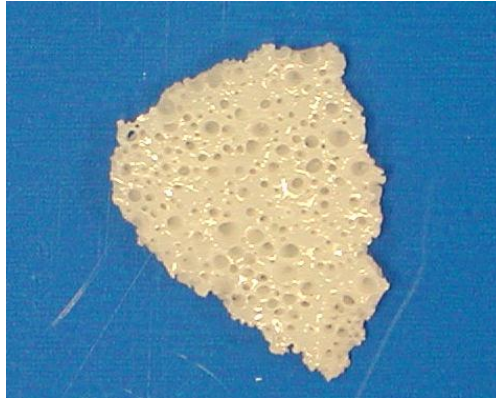


Fig. 19: Porous TZ-3Y sample deposited on wax electrode with differing pore size

In addition to that, a protocol for filling up the pores of a porous layer was developed. The aim of filling up the pores of a porous layer with a dense layer is to create inner defects in a controlled way. The goal is the optimisation of the mechanical properties. Like the TZ-3Y-alumina layer samples, this trial was just performed on the titanium electrode.

The pores were filled with a non-stabilized zirconia powder, TZ-0.

Table 9: Electrical parameters for samples with filled pores

EPD filled pores on Ti electrode		
	Tension (V)	Time (min)
TZ-3Y-ethanol	80	10
TZ-0-water	60	15
TZ-3Y-ethanol	80	30



Fig. 20: TZ-3Y sample with TZ-0-filled pores (deposited on titanium electrode)

Tentatively, this trial seems to be successful.

It still has to be investigated in detail with a SEM, if a filling up of the pores really took place. If this is ascertained, of course, mechanical tests need to be performed.

4.3.4. Samples for mechanical testing

As mentioned before, the actual electrode material used is aluminium foil fixed to a plastic plate with double-sided adhesive tape.

The aluminium foil electrodes used ultimately were 1.5 mm thick, 30 mm wide and 114 mm long.

An enormous advantage of the electrode material was the fact that the sample separates automatically from the electrode during the drying process (figure 23).

This is a process that has yet to be fully understood and which will be a matter of investigation in the future.

The samples are dried in an ethanol atmosphere. With ethanol's slower evaporation, the samples do not crack on the electrode during the drying process.

Additionally, the samples need to be cut at the edges of the electrode to give the sample the opportunity to shrink during drying in order to avoid the development of stresses. Otherwise cracks develop.



Fig. 21: TZ-3Y sample on aluminium foil electrode in ethanol atmosphere

The production protocols for single TZ-3Y and TZ-8Y layers, and 3Y-8Y layered samples were produced on this final electrode material. In contrast to the single-material samples, the 3Y-8Y layered samples do not need to be dried in an ethanol atmosphere, because they are already quite dry when removed from the EPD bath due to water withdrawal during the deposition process. Consequently they do not crack.

In final trials we reshaped the electrode according to the geometry needed for mechanical testing.



Fig. 22: Samples on special shaped aluminium foil electrode in an ethanol atmosphere



Fig. 23: TZ-3Y sample detaching from aluminium foil electrode

We wanted to avoid unnecessary manual treatment, which could lead to deformation and successively to the development of defects.

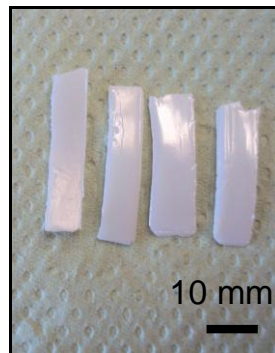


Fig. 24: Single TZ-3Y samples after sintering for mechanical testing

4.4. Sample inspection using scanning electron microscopy (SEM)

4.4.1. Alumina-zirconia layers

Figure 25 shows zirconia-alumina layers.

The layers can be readily distinguished from each other. The pictures were made with a SEM in the backscattering modus. This is why the two materials can be distinguished well from each other.

The last figure clearly shows the difference in the particle size of the alumina and the zirconia powders.

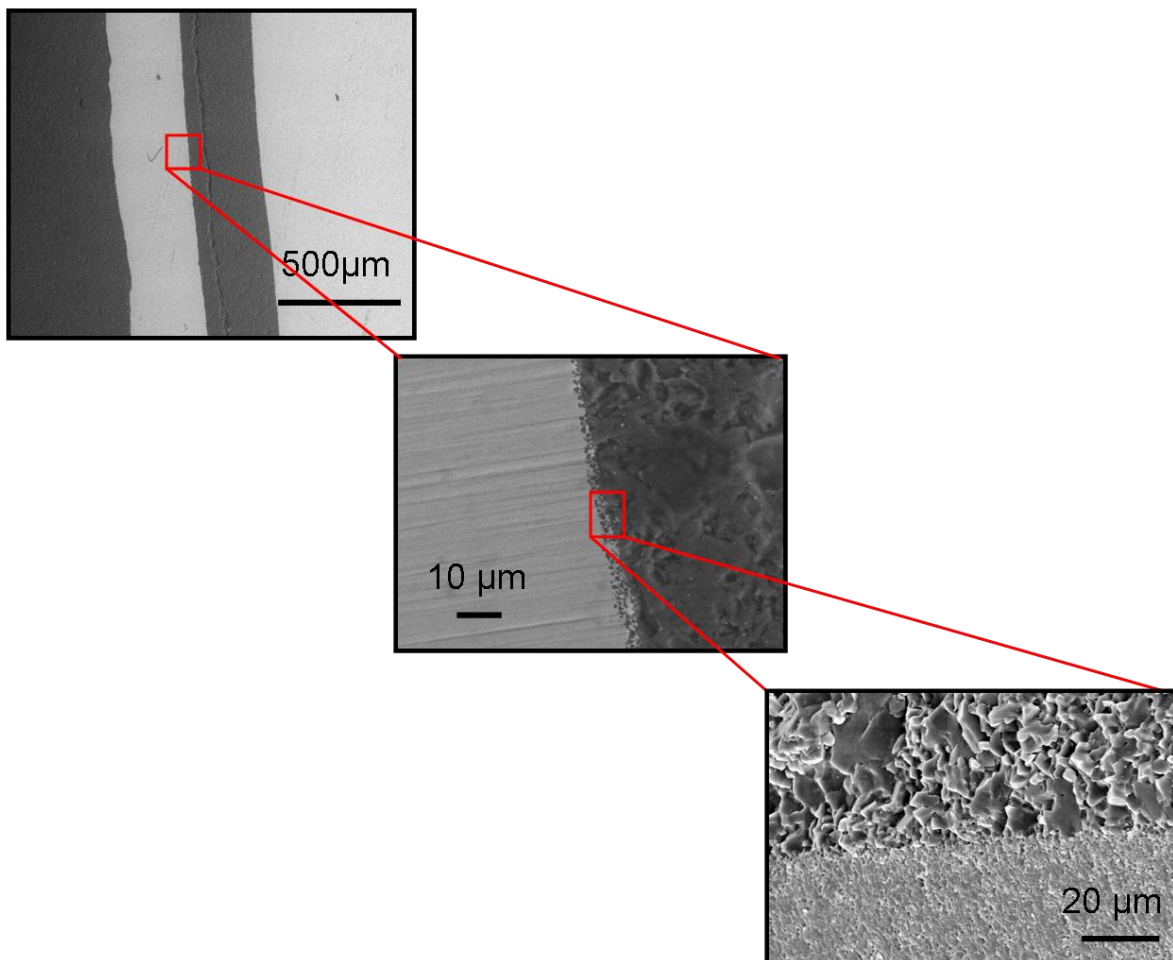


Fig. 25: TZ-3Y/alumina layers

It can be seen that the particles in both materials are densely deposited. Besides, they are distributed homogeneously.

The surface of the alumina layers shows more inhomogeneities than the zirconia layers.

This may be due to the bigger particle size of the alumina powder.

A larger magnification of the alumina-zirconia interface shows an alumina and zirconia particle “interlocking”, which might also be attributed to the difference in the particle size of the two materials (figure 26).

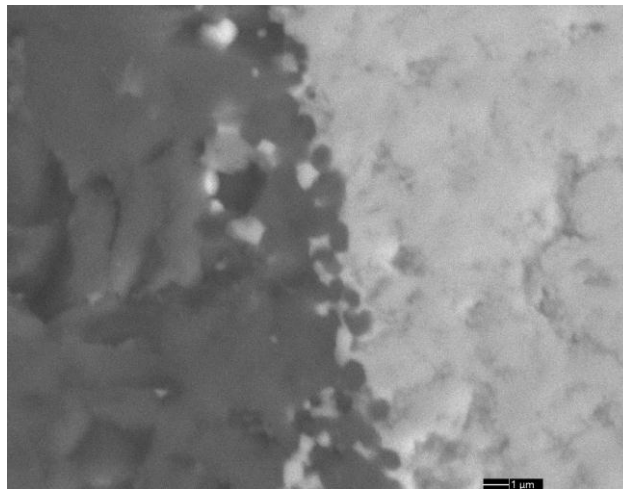


Fig. 26: Interlocking at TZ-3Y/alumina interface

4.4.2. TZ-3Y/TZ-8Y layers

Figure 27 shows TZ-3Y/TZ-8Y zirconia layers. Before inspection, the samples have been embedded, cut and the surface to be inspected was polished in order to obtain better photographs. Without the polishing procedure, the layers were not perceptible. As can be seen, the different layers have a similar thickness and are parallel.

The layer interface is clearly visible as well.

The similarity of the two materials, e.g. particle-size, is apparent.

Besides, both materials are deposited homogeneously. A homogeneous particle agglomeration is achieved in the deposition process.

Higher magnification shows that the grinding protocol needs to be improved, as scratches from the grinding process are visible in the top layer. There is a clear separation between the layers' different materials.

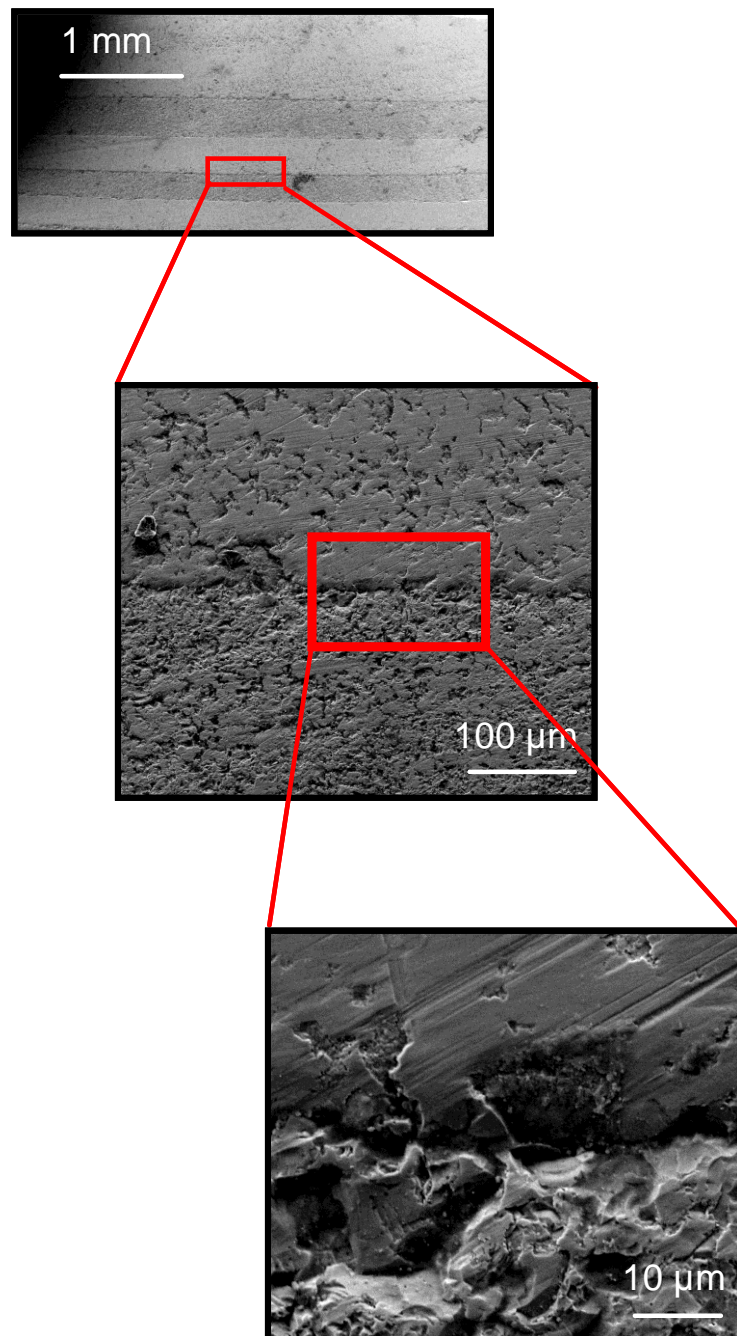


Fig. 27: TZ-3Y/TZ-8Y zirconia layers

4.4.3. Porous samples – first trials

Figure 28 shows a SEM picture of a porous sample with filled pores. Cracks that developed during drying, are perceptible. The inhomogeneous distribution and the varying pore size are clearly visible. Some cracks pass directly through the pores and are not deflected, others seem to be deflected.

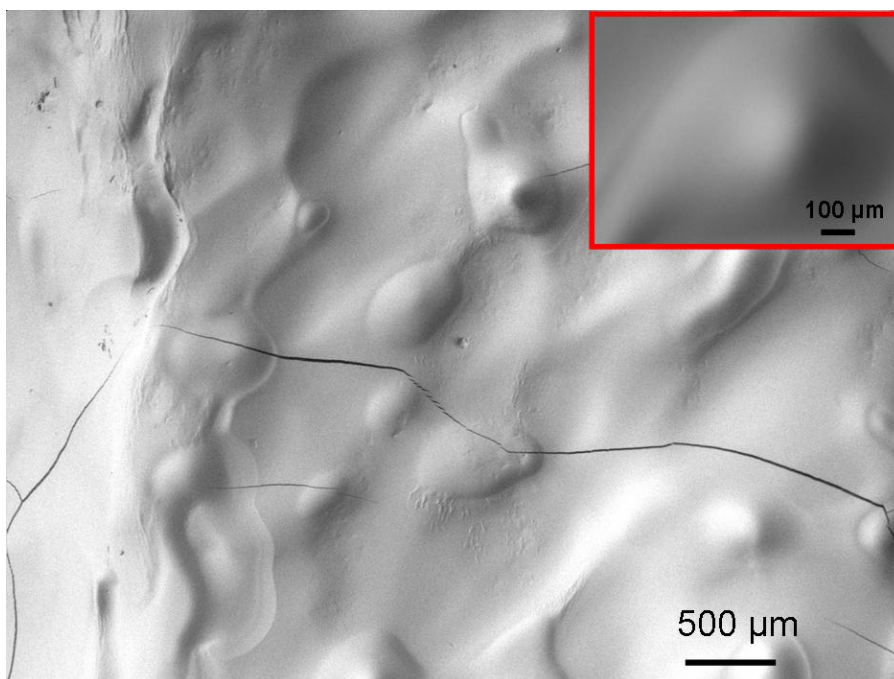


Fig. 28: TZ-3Y sample with TZ-0 filled pores deposited on titanium electrode

The inset shows a close-up SEM figure with a magnification of a filled pore. Even though the picture is not perfectly focused, it is clearly visible, that the pore is filled.

4.5. TZ-3Y/TZ-8Y multilayered sample preliminary mechanical testing

After the sample preparation, they were subjected to mechanical testing. It should be mentioned that the values obtained are just preliminary. The intention was to test if the samples produced by EPD are good and reliable and if the results obtained by mechanical testing are comparable to the ones which can be found in literature.

4.5.1. Vickers hardness

An indent in the TZ-3Y sample is shown in figure 29. A homogeneous and level surface can be seen. Nevertheless, there are some scratches visible, showing that the polishing process probably needs to be improved. Yet, the surface quality was sufficient for the indentation tests performed.

The indent shows a symmetrical shape. There are no detectable cracks that evolve from the corners of the indent-pyramid. The indentation load was 1 kg.

It has to be mentioned that the samples that were tested were resintered after the polishing process and before being subjected to mechanical testing. The zirconia particles transformed to the monoclinic phase due to the grinding and polishing process. The second heating process induces the phase transformation back to the tetragonal phase.



Fig. 29: Indent on TZ-3Y single layer

As shown in figure 30, the average hardness of the TZ-3Y samples is 17.6 GPa. The values given in literature are HV 0.1 1200 [17]. This is equivalent to 11.77 GPa.

As can be seen, the hardness of our samples is higher.

The fact that there is no significant difference between the indents shows that the measurements that we performed are reliable.

It can be said that with the electrophoretic deposition, we are able to produce TZ-3Y zirconia samples with a high hardness.

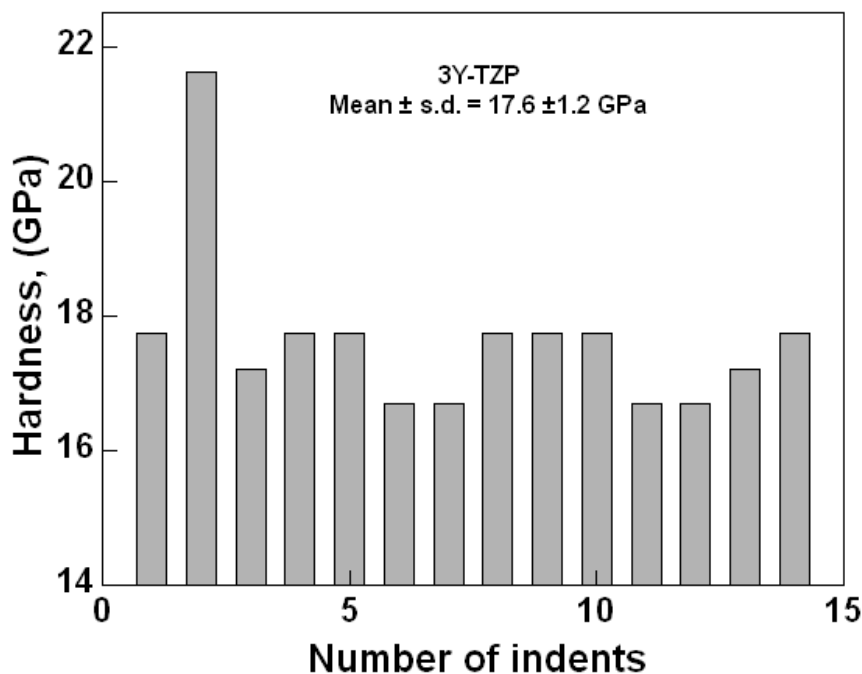


Fig. 30: Hardness TZ-3Y indentation

In figure 31 an indent of the TZ-8Y samples is shown. It is clearly visible that the picture was harder to evaluate, than the TZ-3Y picture.

The indent does not show an exact geometry. Of course, this made the measurement of the indent more complicated.

This is also the reason why the number of indents is smaller in the column diagram for the TZ-8Y samples, than for the TZ-3Y samples. Not all indents were able to be measured. Only twelve values were evaluable.

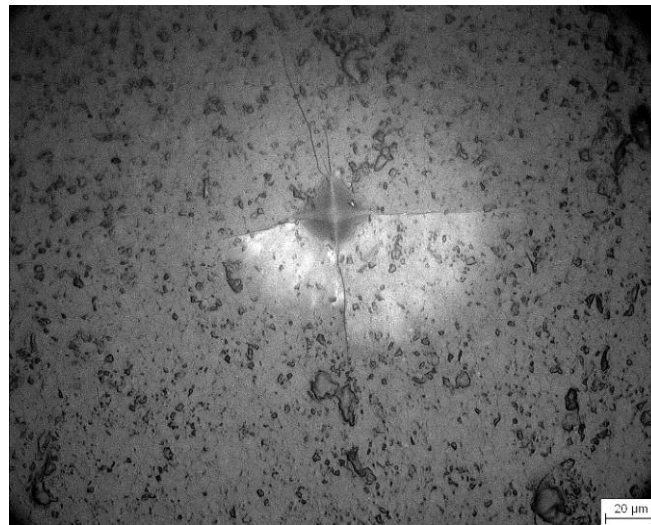


Fig. 31: Indent on TZ-8Y single layer

The great variation in the shape of the indent also explains the wide variation of the hardness values seen in figure 32.

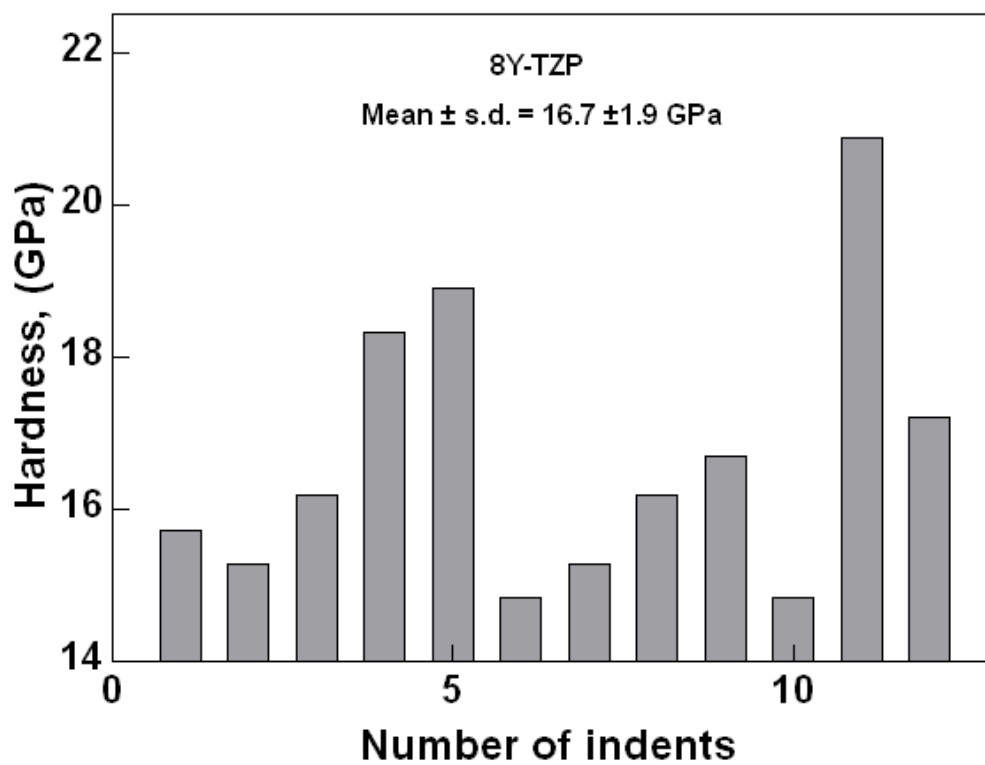


Fig. 32: Hardness TZ-8Y indentation

The hardness ranges between 15 GPa and 21 GPa. The average is 16.7 GPa.

Cracks were developing in all indents made on the TZ-8Y samples, even though the applied load was the same, e.g. 1 kg, in comparison to the TZ-3Y samples. This leads to the assumption that the TZ-8Y samples may be more brittle, because, as can be seen well in the box-plot diagram, there is no significant difference in the hardness of the two materials.

It should be mentioned, that the TZ-8Y samples seem to have a greater plasticity than the TZ-3Y samples. They tend to bend more before breaking. This could also explain the wide variation in hardness of the material.

Even though the deviation for the TZ-3Y and TZ-8Y is quite similar (+/- 1.2 GPa for the TZ-3Y and +/- 1.9 GPa for the TZ-8Y), it is obvious, that the values for the TZ-3Y show a more homogeneous distribution than the TZ-8Y values.

Due to the wide variation of the hardness of the indents for the TZ-8Y, the variation in figure 33 is bigger for the TZ-8Y samples and the hardness seems to be less.

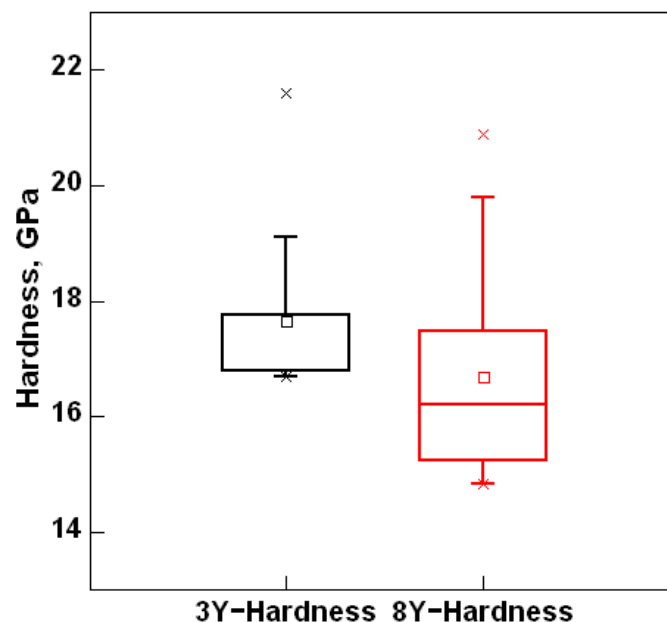


Fig 33: Hardness of TZ-3Y and TZ-8Y single layers

Indents were made in the TZ-3Y layer, TZ-8Y layer or at the layer interface for the TZ-3Y/TZ-8Y layered sample,

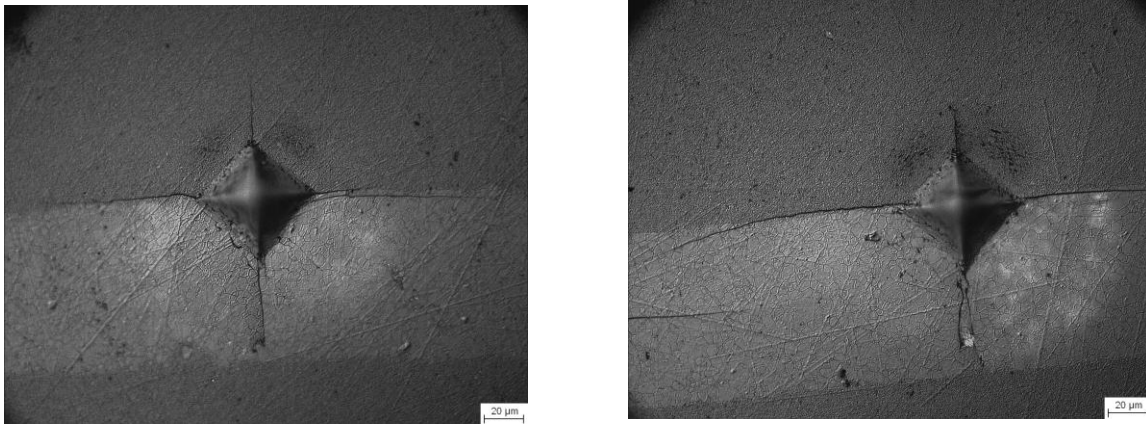


Fig. 34: Indents at TZ-3Y/TZ-8Y layer interface

Horizontal cracks, which develop from the edge of the indenter, mostly grow through 8Y layer or between the interface between 8Y and 3Y layers. In a few other cases cracks develop through the 3Y layer.

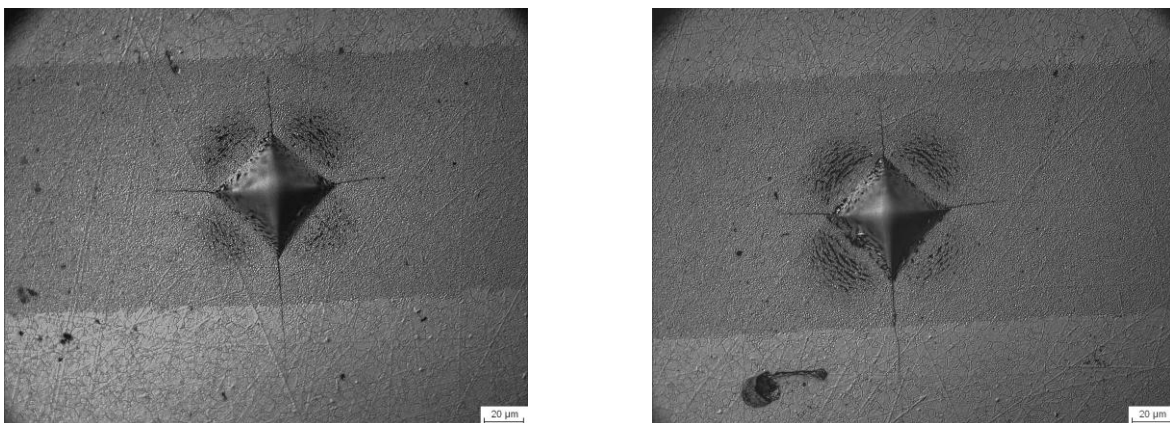


Fig. 35: Indents in TZ-3Y layer:

The cracks are visibly shorter when the indents were performed on the TZ-3Y layer. Cracks were usually passing through the 8Y layer when the indent was placed close to the interface

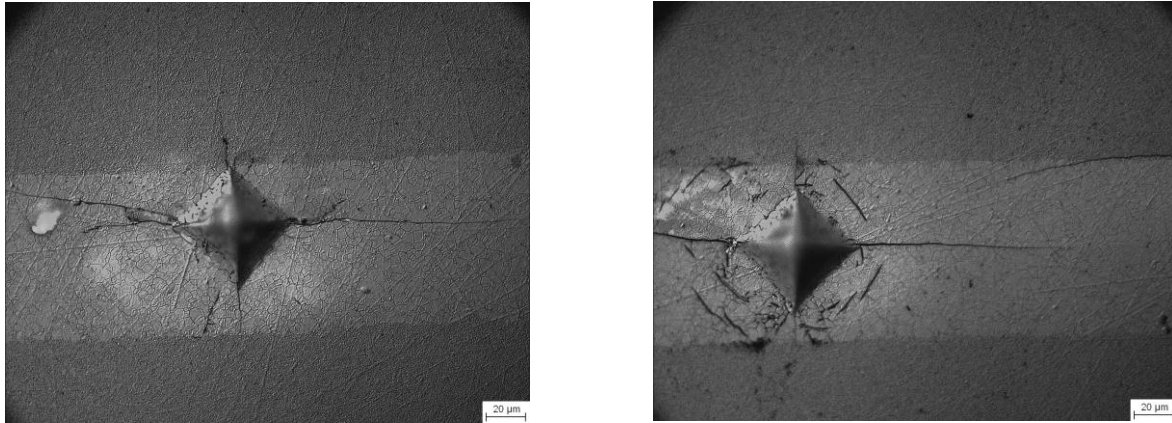


Fig. 36: Indents in TZ-8Y layer

The horizontal cracks are very long when the indents are placed on the TZ-8Y layer. Depending on the position of the indenter, the vertical cracks either grow through the TZ-3Y layer, or are stopped from growing in the TZ-3Y layer at the interface. The cracks that pass from the TZ-8Y to the TZ-3Y layer are much shorter than the cracks passing from the TZ-3Y to the TZ-8Y layer.

4.5.2. Nanoindentation

No significant difference in the hardness between the TZ-3Y and TZ-8Y can be determined in the data obtained by the software. This fact corresponds to the results that we obtained with the Vickers indentation test. The hardness values range between 18 GPa and 21 GPa for both the TZ-3Y and the TZ-8Y. These correlate with the values from the microindentation test.

The values for the TZ-8Y show a bigger deviation than these for the TZ-3Y.

This was also observed in the Vickers indentation tests.

It seems that the TZ-8Y samples are more difficult to evaluate, as the pictures from the microindentation were difficult to analyze. This needs to be further investigated in the future.

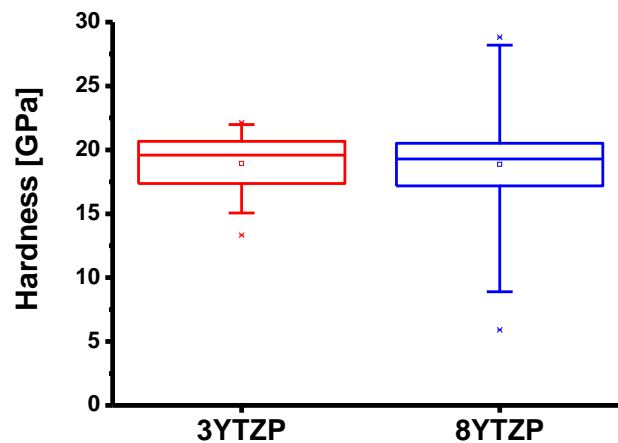


Fig. 37: Nanoindentation hardness

The E_r is also in the sample value range for the TZ-3Y and the TZ-8Y.

It is around 230 GPa, which is consistent with the values found in literature. These are 160-240 GPa for ZrO₂ [51].

Summarizing, it can be concluded, that the preliminary results obtained point in the right direction and are indeed promising. Of course further investigation has to be performed in the future in order to analyze the details in the production process for the EPD samples and to further develop and improve the production protocol.

5 Discussion

Ceramics for dental applications have attracted significant interest in recent years. The optimization and fabrication of dental ceramics is in the centre of discussion and a subject of investigation by many research groups.

The DFG project, which this work is part of, is focused upon increasing the toughness of ceramics by creating hierarchically structured ceramic constructs.

EPD has been pointed out in literature as a suitable technique to create different shapes, structures in different dimension ranges (μm , nm) or combinations of different materials (composites) [2, 33]. Moreover, the interest in ceramic processing by EPD has increased recently [33]. In this sense, within the dental field, EPD has been widely investigated as a method to produce ceramic coatings on metallic dental implants [3, 52]. In addition, the EPD of ceramics for the production of dental crowns and bridges has also been investigated by some research groups. Particularly Moritz *et al.* [37] and Clasen *et al.* [13] studied EPD and its application for the production purposes of dental crowns and bridges. In both groups the tooth-shaped plaster stump serves as an electrode. The deposition takes place directly on it. Afterwards, the three-dimensional ceramic construct is sintered. Finally, the core of the crown needs to be veneered.

An enterprise that is already using a modified EPD system is WOL-Dent GmbH with the WOL-CERAM®-system. It is a patented system, which combines EPD and glass-infiltration [30]. The plaster stump also serves as electrode. The big difference is, that, in contrast to the protocol of the above mentioned research groups, the ceramic body is glass-infiltrated after sintering. Thanks to the direct deposition on the tooth-shaped plaster stump a very precise fitting of the ceramic crown can be accomplished. This is essential for the crown's quality and durability in the patient's mouth.

An EPD set-up was designed and fabricated in this work to perform laboratory experimental work to investigate the potential, advantages and disadvantages of this technique to create hierarchically structured ceramic constructs for dental applications. The main ceramic used to perform the trials in this work was yttria-stabilized zirconia. The effect of layering zirconia with alumina or zirconia with different amounts of yttria

was investigated. According to literature about EPD of ceramics for several applications, this technique may allow us to control the structure of the ceramic crown at different levels of hierarchy, e.g. macrostructure (pores, layers), microstructure (grain size), or crystallographic phase (e.g. tetragonal, monoclinic or cubic zirconia). This may have a positive effect on the quality and reliability of the product. As already mentioned in the introduction, currently the most common method of producing ceramic caps for dental crowns and bridges is machining from presintered blocks. This procedure is quite time-consuming. The dental technician needs to wait for the milling machine to finish in order to continue the work. In contrast to that, the EPD process is less time consuming. The deposition periods range between 10 min and 20 min [37]. This is a substantial advantage, as the deposition takes place directly onto the plaster stump, a very precise fitting of the crown can be achieved. Fewer corrections performed by the dentist are necessary to fit the crown into the patient's mouth. This is particularly advantageous in the case of zirconia crowns, because mechanical processes, like grinding, usually have a negative influence on the mechanical properties of the zirconia crown, that may tend to crack spontaneously.

As already mentioned in the introduction of this work, zirconia ceramics have gained interest in dental applications due to their good aesthetic quality. A completely natural appearance of the artificial crown or bridge fulfils the patient's desire for invisible dental restorations. Moreover, specifically its relatively high toughness makes it a particularly practical material in dental applications, as the material has to stand the high masticating forces in the mouth. The high toughness is attributed to a phenomenon popularly known as transformation toughening. A propagating crack induces the transformation of the zirconia particles from the metastable tetragonal phase to the monoclinic phase. This is accompanied by a volume increase, which impedes crack propagation. Aside from the $t \rightarrow m$ phase transformation, there are many other factors that have been claimed to influence the crack stopping between ceramic interfaces [53]. Moreover, recent investigations by Fratzl *et al.* [54] point out that in natural biomaterials, interfaces with a ratio of elastic moduli greater than about 5 lead to effective crack stopping. From the structural point of view, specific microstructural features in the ceramic, e.g. pores in a specific size and/or shape [55-57], or interfaces between materials with different grain size [48, 58, 59] can initiate mechanisms, which lead to crack deflection or even crack stopping. Figure 38 shows a schematic view of the

layering of materials with different microstructures, i.e. grain size (figure 38a) and microporosity (figure 38b).

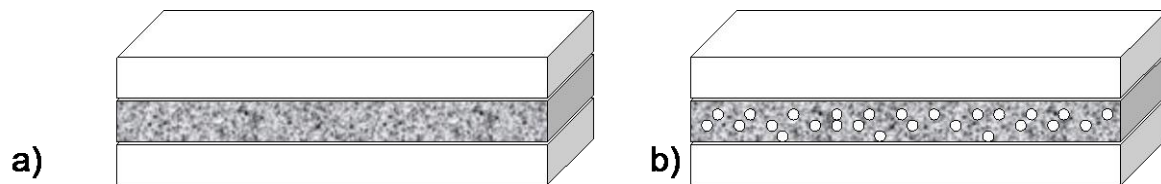


Fig 38: Microstructures in layered samples (a) grain size and b) microporosity)

In the present work the layering of TZ-3Y and TZ-8Y, or TZ-3Y and alumina powders was performed and graded layered ceramic materials were produced. Moreover, initial trials layering porous and dense layers were performed. We experimented with different levels of hierarchy. The macrostructure is controlled by the combination of dense and porous layers. The microstructure (e.g. grain size) is controlled by layering zirconia and alumina and the crystallographic phase is controlled by layering TZ-3Y and TZ-8Y.

Ceramic layering has been an object of investigation since the 1990s. Particularly the layering of zirconia and alumina has been in the centre of the discussion. It is shown that in direct comparison of the pure material and the layered structure the laminates show better resistance to damage than the pure material [60, 61]. Sarkar *et al.* produced electrophoretically deposited alumina-zirconia layers in the early 1990s [62-64]. Both powders, alumina and zirconia, were dispersed in ethanol. Crack deflection was observed at the interfaces approaching the zirconia layer [65, 66]. Ferrari *et al.* worked with the layering of pure zirconia and alumina as well in the late 1990s [45, 46]. The layers were produced by EPD with watery suspensions. The obtained layers showed a more porous structure. Alumina and zirconia layering is still an object of research currently [67]. Bermejo *et al.* have worked with a layer design consisting of alumina-zirconia mixtures in order to improve the mechanical properties of the ceramic samples. The multilayered samples are produced by slip casting. The layers consist either of a mixture of alumina and tetragonal zirconia powder or a mixture of alumina and monoclinic zirconia powder [68, 69]. Due to this difference in the phases of the zirconia particles, which is accompanied with an increase in volume for the tetragonal zirconia particles, compressive stresses develop in the layered structure that may also

impede the propagation of cracks [59]. They show that the fracture energy of a multilayered material is six times higher than that of monolithic alumina materials [68]. The production of laminated structures with compressive residual stresses within the surface regions has been proven to be a suitable method to obtain composite materials with superior tribological properties [70].

Zirconia-alumina laminates were successfully produced by EPD in this work. The interfaces between the different microstructures in the zirconia and alumina layer present an “interlocking” type of arrangement of the alumina and zirconia particles as shown in figure 26. The initial particle size of the alumina particles is larger than that of the zirconia particles. Probably the larger alumina particles cause the smaller zirconia particles to displace. This leads to an interlocking of zirconia and alumina particles at the layer interface. Apart from the zirconia-alumina layered structures, some recent studies have focused on the investigation of composites combining only zirconia with different amounts of doping [71, 72]. Zirconia stabilization to its tetragonal or cubic phase by just changing the amount of doping provides the prospect of attempting to combine the properties of these two materials. This is the idea behind the design of the TZ-3Y and TZ-8Y multilayered samples produced in this work. In comparison to the alumina and zirconia (TZ-3Y) layering, the interface of the TZ-3Y/TZ-8Y layers appears to be sharp even though the final grain size in the TZ-8Y layer seems to be bigger than the final grain size in the TZ-3Y layer (figure 27). In contrast to the alumina powder, the initial particle size of the TZ-8Y powder correlates with the initial particle size of the TZ-3Y powder. The interlocking phenomenon probably depends upon the initial particle size of the powders, which directly influences the arrangement of particles during the EPD process. The final grain size of the TZ-8Y layer might change due to particle “clumping” or during sintering. Furthermore, we developed a different approach to ceramic layering. By layering TZ-3Y and TZ-8Y (e.g. tetragonal and cubic zirconia) the crystallographic phase is controlled.

The EDX analysis shows a clear difference in the yttria content of the TZ-3Y and TZ-8Y layers and confirms a layered structure. It shows that in contrast to the zirconia-alumina layers, no interlocking takes place between the two zirconia layers (figure 39).

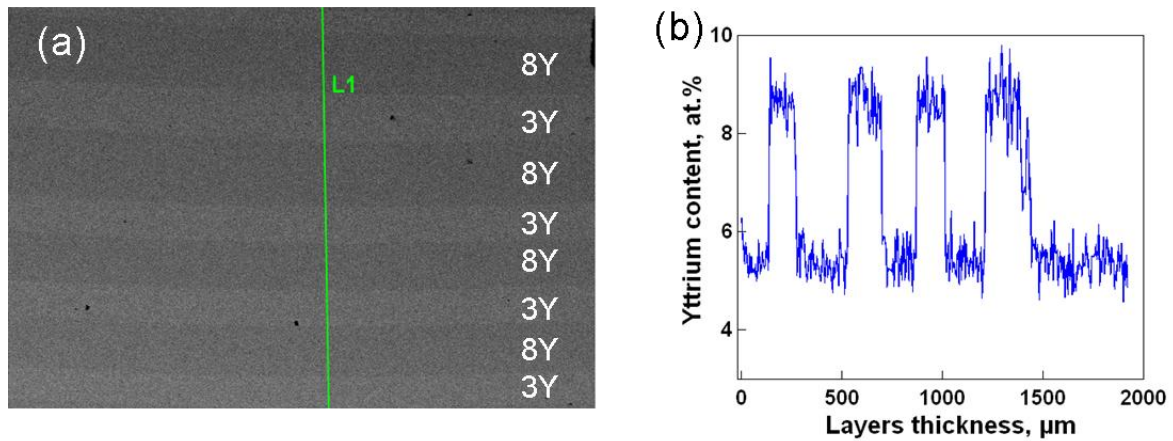


Fig. 39: EDX analysis TZ-3Y/TZ-8Y layer

The XRD analysis proves a mainly tetragonal phase in the TZ-3Y layer (figure 40a) and a mainly cubic phase for the TZ-8Y layer (figure 40b). In both layers an amount of monoclinic zirconia particles is present.

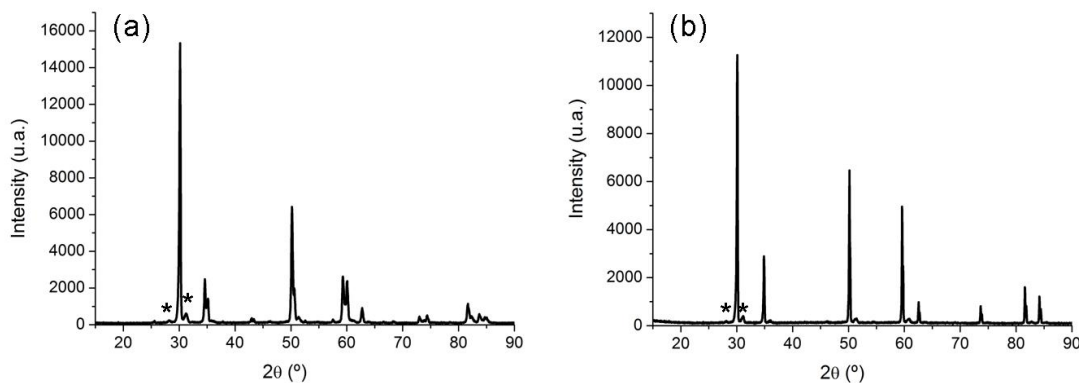


Fig. 40: XRD analysis: particle phases for a) TZ-3Y and b) TZ-8Y

The TZ-8Y layer contains cubic zirconia particles, which do not undergo a phase transformation in the case of a propagating crack. The TZ-3Y layer contains tetragonal zirconia particles that undergo the $t \rightarrow m$ phase transformation. The phase transformation of the tetragonal zirconia particles is accompanied by an increase in volume. This expansion of the TZ-3Y layer in the ceramic construct may cause the development of compressive fields in the TZ-8Y layer. Thus, the TZ-3Y layers probably develop tensile stresses (i.e. tensile layers), whereas the TZ-8Y develop compressive stresses (i.e. compressive layers). Indeed, Figure 34 shows that the crack along the interface tends to deflect towards the TZ-8Y layer. The indents performed on the TZ-3Y

show a significantly different length of the cracks propagating through the TZ-3Y layer to the ones propagating towards the TZ-8Y layer. However, it has to be considered that the short propagation of the crack in the TZ-3Y layer (figure 35) may be due mainly to the crack-stopping mechanism in the layer itself ($t \rightarrow m$ toughening mechanism) and not to the interface. To better understand the toughening mechanisms occurring in the 3Y-8Y multilayered specimens, further investigation will be performed. Moreover, the optimal thickness in the 3Y-8Y multilayered design should be studied. In this sense, the previous work on the effect of the compressive layers in layered ceramics performed by Bermejo *et al.* [59, 69] should be considered.

Additionally, the fact that scratches are present on the surface of the ceramic samples has to be taken into account. However, these scratches do not seem to influence the crack propagation through the layers' interface in a significant manner. For instance, in figure 34 (right hand picture) the crack emerging from the right corner of the indent passes through a visible scratch without any clear effect, and moreover, the path of this right hand crack shows the same behavior as the crack emerging from the left hand corner where no visible scratch is present.

It should also be considered that in Y-TZP ceramics that are exposed to fluids (i.e. body fluids), when cubic grains are present in the tetragonal TZ-3Y layer, yttria is attracted to the cubic grains leading to a lack of yttrium at the tetragonal grains [73]. As the particles strive to achieve the monoclinic equilibrium stage, the usual $t \rightarrow m$ phase transformation takes place and microcracking occurs causing failure [74]. It has been recently pointed out that due to this effect the presence of cubic grains has a negative influence on the mechanical properties of zirconia when used for biomedical applications [73]. This phenomenon is known as "low temperature degradation (LTD)". We cannot be sure how the LTD influences the interface in our TZ-3Y/TZ-8Y system. This will have to be investigated in the future. To avoid this phenomenon, another dopant e.g. ceria, could perhaps be used [74].

The application of EPD to produce reliable and reproducible ceramic samples depends upon controlling various parameters. It is particularly difficult and time consuming to adjust these in order to obtain a reproducible ceramic sample.

The scheme in figure 41 gives an overview of the parameters and their influence on the EPD process.

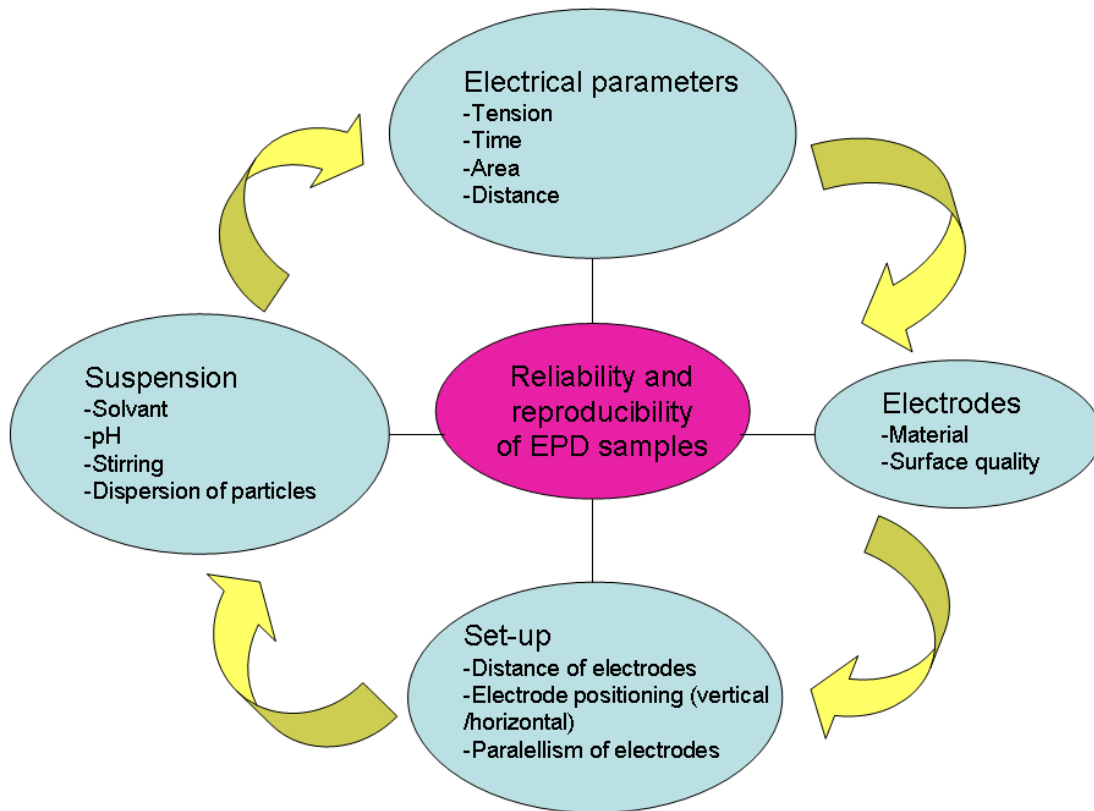


Fig. 41: EPD parameters influencing the quality of the ceramic sample

The set-up in this work was developed according to the basic composition of an EPD cell. The electrical parameters, e.g. tension and time depend upon the suspension parameters, the electrode material and the set-up, e.g. the distance between the electrodes. This is why they differ significantly throughout literature.

The initial parameters applied to our EPD process were altered and adjusted according to our needs and set-up (table 4). A fixed and parallel position of the electrodes was accomplished. This is essential to guarantee the reproducibility of the ceramic samples. The electrodes were fixed in a vertical position. The term “vertical set-up” refers to the positioning of the electrodes and not to the direction of the electrical field in this work. With this set-up samples with a particularly homogeneous particle distribution and sufficiently consistent layer thickness were obtained (see figures 21-23 and 25, 27).

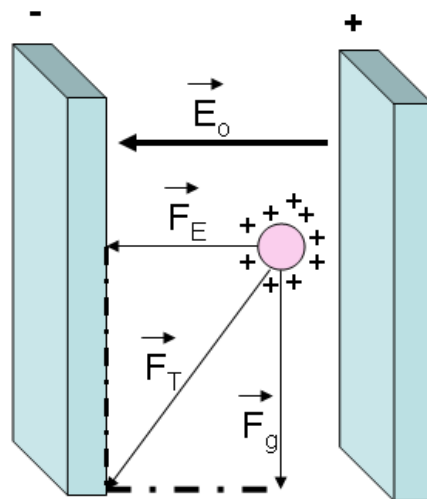


Fig. 42: Forces influencing the motion of the ceramic particle

The motion of the ceramic particles that are dispersed in the suspension, is influenced by gravity (F_g) and the electric field strength (F_E). The particles do not follow the horizontal path of the electrical field due to gravity. They follow F_T , which results in a ceramic particle segregation in the suspension (figure 42). The thickness of the deposited layer differs throughout the deposit as a result. The deposit is thicker at the bottom. This segregation phenomenon due to gravity is not often described in literature even though in general, vertical set-ups are used [75-78]. Maca *et al.* [76] mention the problem of suspension segregation and its negative influence on the quality of the deposit. However, the particle segregation depends upon the time. Maca *et al.* [76] avoid segregation by stirring the suspension every 30 min and so take advantage of the segregation's dependence on time. If the time used to produce the ceramic sample is inferior to the significant particle segregation in the suspension, it is not a problem. Nevertheless, although this is not an optimal procedure, if the particle segregation had a negative influence on the final quality of the ceramic deposit, it is possible to cut the deposit manually and to remove the thicker part. Usually only small and magnified parts of the ceramic samples are shown in literature. Yet, this manual treatment is not optimal, because invisible cracks or flaws could develop which might influence the mechanical testing and distort the values. Probably a set-up, in which the electrodes are fixed in a horizontal position, is a better way to avoid the segregation phenomenon. The existing set-up demands a manual dipping and withdrawal of the electrodes from the

suspension. The speed of the electrodes during dipping and withdrawal cannot be controlled. It is possible that, the dipping speed may have an influence upon the deposited layer. In addition to that, the deposition period cannot be determined precisely with manual dipping/withdrawal and manual time measurement. This is why, as a part of the SPP1420 DFG project, we are currently working on the development of an automated EPD set-up with control of the dipping/withdrawal speed and time measurement. Besides, a horizontal electrode positioning is also being developed in order to avoid a segregation of the particles in the deposited layer.

Another factor, which causes undesirable effects in the deposit, is the constant magnetic stirring. However, in trials performed in this work, it was not possible to avoid a slight magnetic stirring in order to minimize the particle segregation due to gravity and keep them well dispersed in the suspension. This stirring leads to suspension movement that may influence the layer in different ways that may cause the appearance of aleatory defects and pores. In this sense, small bubbles developed during the deposition process creating undesired pores in the layer. The development of pores in the EPD of ceramics will be addressed in more detail later on. Besides, we cannot be completely sure whether all the particles are well dispersed and are really deagglomerated. Thus, the stability of the suspension needs to be improved to try to avoid magnetic stirring.

The composition of the suspension differs a lot throughout research groups. Usually many additives, for example binders are added to the suspension. As these binders and additives usually are quite expensive, the ceramic sample costs are increased. Also, the more basic the composition of the suspension, the fewer parameters can influence the EPD process and the less complicated it is.

The suspension's essential parameters are pH and particle surface charge. The pH directly influences the particle surface charge in the suspension and so determines their velocity. The pH for zirconia suspensions that is usually found in literature is acidic. It ranges between 3.5 [78] and 5.7 [62] usually. More tests, e.g. measurement of the zeta potential, need to be performed in order to analyze the precise suspension parameters. According to Chen [79], who studied the surface charge of alumina particles in ethanol suspensions, the suspension is most stable at a pH of around 2.2 and least stable at a pH of around 11. The suspension pH used in the experiments performed in this work

ranges from around pH 5 to 6. Conductivity measurements of the TZ-3Y, TZ-8Y and alumina suspensions show the highest conductivity for the TZ-8Y suspension (TZ-3Y 48.5 μ S, TZ-8Y 212 μ S and the alumina suspension 0,6 μ S). This correlates with the lowest tension of 10V applied for the TZ-8Y suspension.

Table 10: Parameters of the suspensions

	pH	Conductivity (μS)
TZ-3Y	6.35	48.5
TZ-8Y	5.78	212
alumina	5.34	0.6

According to the results from Chen, it could be practical to lower the suspension pH by adding more acetic acid. Then a measurement of the zeta potential would give information on the ceramic particle velocity and show whether a difference in the velocity of the particles is detectable in the differing suspensions.

The conductivity of the suspension has a direct influence upon the electrical parameters. The higher the suspension's conductivity, the higher the energy efficiency of the EPD process. The most common solvent used in literature is either ethanol [62] or water [46]. But also others like n-propanol [80] are used. The solvent used for this suspension is 96% ethanol. It contains 4% water. In later trials it appeared that this water content was problematic. Occasionally, small bubbles developed during the deposition process that were included in the deposited layer. Undesired pores developed in the layer.

The appearance of undesired pores due to bubble development in the suspension has been long considered as a problem in the field of EPD. Indeed, the appearance of pores is directly related to the H₂- and O₂-development on the electrodes. Moreover, our trials showed an increase in this effect with an increase in magnetic stirring. Different research groups developed set-ups with membranes in order to avoid the appearance of pores [13, 81]. The membrane separates the electrophoretic cell. The deposition takes place on the membrane, whereas the bubbles develop on the electrodes [81]. Consequently, the bubbles cannot influence or inhibit the deposition of the powder particles. A particularly dense powder particle deposition can be achieved only in this

manner. We need to try to control distribution and size of the pores better. A possible way to do so might be by changing the solvent. The use of 100% ethanol might be a satisfactory method. Due to the absence of water the development of bubbles should not take place. However, the atmospheric hydration of the ethanol along with magnetic stirring during the deposition process may still trigger the development of bubbles. Thus, to produce particularly dense ceramic samples, the use of a membrane cell has to be considered for future trials. On the other hand, porous structures produced by EPD have been attracting increased interest in recent years as well. The porous materials are used in the application of bioactive scaffolds, drug delivery systems or orthopaedic implants [3]. In this work, the approach to porous ceramic structures was the graded ceramic production. Similar to the layered ceramic structures, the creation of interfaces in a ceramic sample using a combination of porous and dense materials and a combination of a stabilized and a non-stabilized zirconia powder (figure 28) is designed to trigger crack deflecting or energy dissipating processes, which should then blunt or even terminate the propagation of cracks. Pores develop due to hydrogen and oxygen development in watery suspensions and also in suspensions prepared with 96% ethanol at the electrodes once the decomposition voltage of water is exceeded [13]. These bubbles are incorporated into the ceramic layer on the electrode [13]. At this moment we are not able to control the size and distribution of the pores, which is necessary to develop reproducible samples. Additionally, constant magnetic stirring, which is necessary for the stabilization of the suspension, might create small pores. The constant motion of the suspension might lead to particle withdrawal from the deposited layer. Moritz *et al.* [44] developed methods with which they are able to control the pore size and distribution, by attaching a mesh in front of the deposition electrode. This would be another option for future work. This fact emphasizes the importance of the suspension composition and other parameters influencing the EPD process.

Another essential factor that has to be considered for the EPD set-up is the electrode material. It needs to be conductive as it directly influences the electrical parameters. Moreover, easy removal of the deposited ceramic sample from the electrode is desired. Unnecessary manual treatment needs to be avoided as it can influence the quality of the ceramic sample. In literature, a variety of materials is used for electrodes. Stainless steel [66, 82] or platinum [44-46] are just two among many others. The final electrode material used in this work is aluminium foil. It appeared to be particularly convenient, as

it is very conductive and therefore energy efficient. Additionally, the deposited layer separates without any additional mechanical manipulation from the foil (figure 23). This is a significant advantage, because the removal of the deposited ceramic sample from the electrode created a crucial problem. Many research groups tried to cover the electrodes with conductive paper or plastic [63] or sputter the electrodes with carbon [82] to facilitate the removal of the ceramic sample. During the development of the set-up of this work, trials with carbon-sputtered titanium electrodes were performed as well. But the sputtering effect did not achieve the desired removal procedure facilitation. Manual removal from the electrode usually resulted in partial damage of the ceramic sample.

Little information is available about the removal of the ceramic sample from the electrode in literature. This might be proof for the importance and difficulty of this procedure. Platinum, which was used in the initial trials, has proven to be too expensive as electrode material. Aluminium is an inexpensive but very conductive material. The tension applied in the deposition process can be very low (e.g. 10V-15V). The energy efficiency is very high, which reduced the costs of the whole production process. Aluminium plates were used as electrodes in the initial trials. No difference could be found between the titanium electrode and aluminium electrode, particularly concerning the removability of the ceramic. Trials performed on stiff polished aluminium plates have shown, that an automatic separation from the electrode does not take place with this material. This is very disadvantageous. This is why the deposition electrode was changed to aluminium foil. The automatic detachment of the ceramic sample from the aluminium foil electrode was a significant advantage. One disadvantage is the fact that the aluminium foil itself is not stable or stiff enough to be dipped into the suspension by itself. It would not be possible to position the electrode exactly parallel. Also, the electrode would move in the suspension during the deposition process due to the induced movement of magnetic stirring. The aluminium foil needs to be attached to a plastic plate carrier. We used double-sided adhesive tape. However, it is difficult to fix the foil perfectly flat on the plastic carrier. Sometimes small wrinkles develop. This irregularity in the electrode results in the development of inhomogeneities in the ceramic sample. This is disadvantageous, as the surface quality of the electrode has a significant influence on the quality of the ceramic layer.

The idea of sputtering the electrode gave us the idea of sputtering very cheap PMMA. Another advantage of the PMMA is its versatility. According to the intensity-time curves shown in figure 15, the electrical behaviour of different sputterings can be analyzed. Comparing the intensity-time curve behaviour of the aluminium and gold- or carbon/gold- sputtered electrodes it becomes evident, that the starting intensity for the TZ-3Y suspension on the aluminium foil electrode and the gold sputtered electrode are similar (approximately 3.5 mA). The starting intensity for the TZ-3Y on the carbon/gold sputtered electrode is lower. This can be explained by the very low conductivity of the carbon/gold sputtered electrodes. The intensity values for the aluminium suspension are generally lower than these of the TZ-3Y suspension. The starting intensity values range around 0.45 mA. Just as for the TZ-3Y suspension, the starting intensity is lower for the carbon/gold sputtered electrode, which can again be attributed to the very low conductivity of the electrode material. Considering the tension that was applied to the aluminium foil electrode and the sputtered electrodes, it becomes evident that the energy efficiency is higher for the aluminium foil electrode. Here, the applied tension ranges between 10V and 30V. The tension needed for the sputtered electrodes ranges from around 80V to 120V. For the alumina suspensions, the exponential decrease, which is expected for an EPD process, is not as explicit as in the other suspensions. This fact occurs in both the aluminium foil electrode and the sputtered PMMA electrode. The alumina particles are bigger than the zirconia particles. The alumina particles cannot be as densely packed. Due to greater inter-particle space, the ceramic layer contains more water. This may cause a more linear curve behaviour due to the constantly higher conductivity. The larger size of the alumina particles can also explain the fact that the intensity of the alumina suspension is generally lower. Even though the sputtered PMMA electrode material is quite cost effective, the fact of the high tension required relativises this advantage. Additionally, the deposition on the aluminium foil (figure 21) seems to provide better, more homogeneous ceramic layers, than the sputtered PMMA electrode (figure 14).

The distance between the electrodes found in literature ranges from 1.0 cm to 2.6 cm [45, 64, 75, 76]. The distance, which has proven to be the most convenient for our set-up was 2,5 cm. The electrodes should not be placed too far apart, because then the electric field (E_0) would become weaker and non-uniform; and therefore excessively high tension values would be necessary. The fact that the tension is different in each

electrode material and suspension should also be taken into account; for example, the higher the conductivity of the electrode material, the lower the tension applied. Thus, a low-priced electrode material with good conductivity is ideal. The optimal tension also has to be adapted to the suspension used, as it will influence particle surface charging. The tension required for the deposition process with the alumina suspension is usually higher, than for the zirconia suspensions. This correlates with the bigger particle size of the alumina powder. In the same way, there is a difference in tension between the 3Y-TZ (crystallite size 26nm, density 1.263 g/cm³) and the TZ-8Y (crystallite size 23nm, density 1.21 g/cm³) suspensions. The tension in the TZ-8Y suspension is lower (10V) than that in the TZ-3Y (15V). No homogeneous layer could be deposited if a higher tension was chosen for the TZ-8Y suspension. The particles may displace already deposited particles due to their very high velocity. This shows the direct influence of the electrical parameters on the suspension.

The powders used for the EPD process are all nanopowders. During the development of the EPD procedure, it became evident, that, when powders with crystallite sizes in the nanometric range were applied, the quality of the ceramic sample was influenced in a positive way. Moreover, it was easier to stabilize the suspension. Differences were already noticeable between the zirconia and alumina powders. If powders with larger particle sizes were used, additives would have to be added to the suspension in order to stabilize it. This is undesirable, because then more parameters would have to be considered and adjusted, which would make the whole process more complicated.

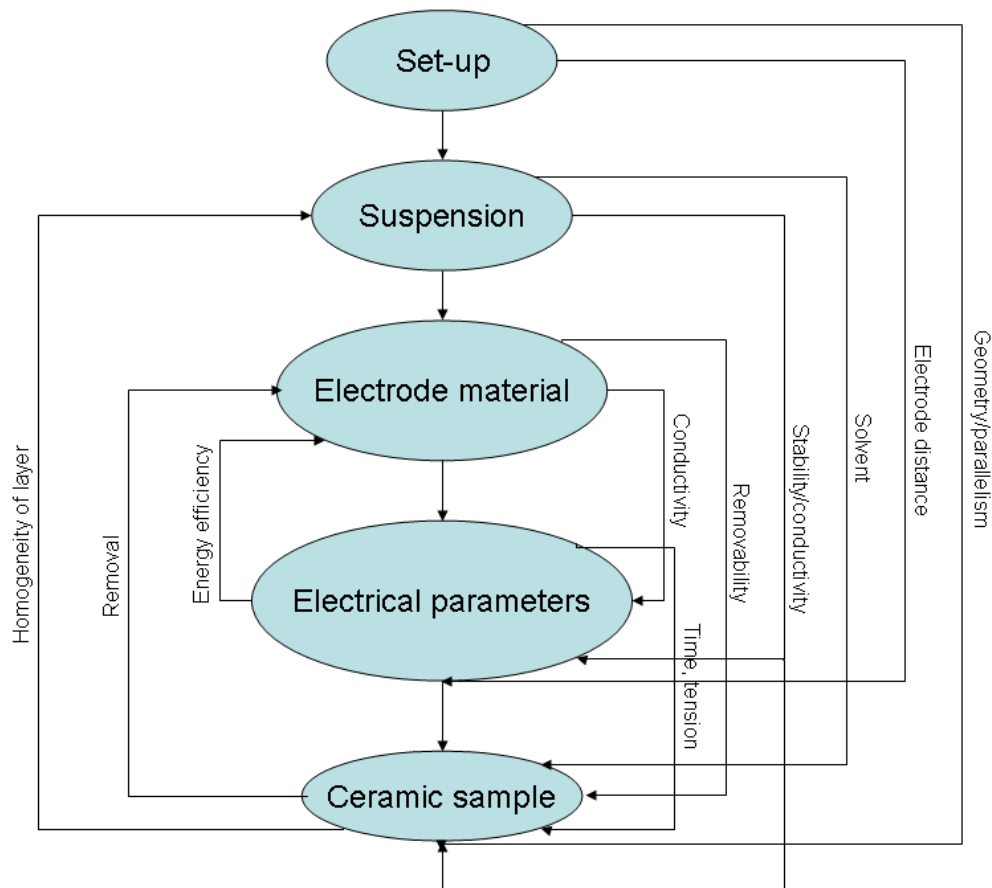


Fig. 43: Influence/dependence of EPD parameters

As a final step the ceramic sample obtained by EPD needs to be sintered. The heating process stands apart from the afore-mentioned parameters. But it has a significant influence on the quality of the ceramic sample. The importance of a graded heating rate is also described in literature. Liang and Blackburn even discovered in their experiments, that major failures in the ceramic sample occur while cooling down from the sintering temperature [49]. Apparently, the different layers become less compliant and exhibit different mechanical properties, e.g. thermal contraction. Additionally, they noted that the higher the number of layers the higher the strength of the sample, because of different crack deflection mechanisms. They claim that a sample's strength is highest when the total number of layers is 5.4 [49]. That is the reason why, it is absolutely necessary that the heating rate is kept particularly low, e.g. 3-5 °C/min [49]. Besides, they keep the thickness of the layers at around 0.3 mm and use a combination of ZrO_2 and Al_2O_3 for the layers in order to reduce stress development. The sintering and cooling process of layered materials also plays an important role in terms of stress

development and hence crack development in the material. As the transformation of ZrO₂ from tetragonal to monoclinic during cooling after sintering occurs spontaneously, the presence of inhomogeneities may increase the local stress concentration that may decrease the mechanical properties of the material. It is assumed that residual stresses start to develop from 1200°C [48]. In this work, the applied heating procedure comprises three sintering programs. These are necessary in order to allow a graded heating rate in different steps. The ovens available did not give us the opportunity to combine in one single heating program this required gradual heating. Reviewing this heating protocol critically, it proved not to be ideal. Due to the three heating programs the samples go through six heating and cooling processes. This may cause stress development in the samples. With an oven that allows its user to program a gradual heating process, exposing the samples to unnecessary cooling and heating periods could be avoided. Otherwise the development of internal stresses, which may influence the mechanical stability of the ceramic samples, cannot be excluded.

A new oven has been acquired recently in association with the DFG project. This oven is able to provide the required gradual heating. New sintering programs will be developed in the future and will be investigated further.

As a general conclusion, the results presented in this work show that, indeed, EPD is a potentially effective technique to create ceramic constructs with several shapes, architectures and hierarchical levels. However, during mechanical testing and in the course of the work, it became evident, that some parameters in the production process still need to be optimized, e.g. automatization of the EPD system, membrane method, heating process, horizontal positioning of the electrodes, grinding process or the stability of the suspension.

Nevertheless, the versatility of ceramic EPD makes it an exciting option for optimal production of ceramic dental constructs such as crowns or bridges.

6 Summary

The application of ceramics for dental purposes is a very important field currently, particularly due to the patient's desire for invisible tooth-like restorations. This is why efforts are made to improve the mechanical properties of ceramics, in order to obtain a reliable material.

In particular, zirconia ceramics are attracting increasing interest for medical applications due to their excellent material properties.

Tetragonal zirconia polycrystal (TZP) ceramics show a relatively high toughness due to a stress induced phase transformation which impedes crack propagation.

Currently, Electrophoretic deposition (EPD) is attracting increasing interest for medical applications particularly due to its cost effectiveness and versatility. This versatility might help to improve dental ceramic appliances such as crowns and bridges. In this sense, the EPD of ceramic particles has already been used in the WOL-CERAM®- system that is being successfully applied in dental laboratories at present.

An individual EPD set-up was developed in this work. The suspensions worked with were TZ-3Y, TZ-8Y and alumina ethanol mixtures in dense samples or TZ-3Y water mixtures in porous samples.

The experimental work performed in this thesis points to the prospect of using EPD to include different structural features in the dental ceramic construct. This might help improve the final clinical reliability.

According to literature, layered ceramics is a promising design for the enhancement of mechanical properties in order to fulfill high mechanical requirements that are necessary in medical applications. This is also why TZ-3Y/TZ-8Y multilayered samples and TZ-3Y/alumina multilayered samples were produced in this work. Moreover, initial trials combining a porous structure and a dense structure were performed.

The samples were subjected to preliminary mechanical testing: Vickers indentation and nanoindentation.

Investigations using scanning electron microscopy (SEM) revealed different types of interfaces in the layered ceramic constructs. The layer quality depends upon the particle

size of the electrophoretically deposited powders. Moreover, different porosity grades were easily achieved with the trials performed in this work.

However, the EPD set-up used in this work should be further optimized in order to obtain a reproducible size and distribution of the pores, for example by developing a new suspension composition and/or a new set-up design.

Even though the EPD protocol needs to be improved, the results point to the fact, that EPD is a potential technique to produce ceramic samples with different shapes and levels of hierarchy.

7 Abbreviation Index

EPD	Electrophoretic deposition
TZP	Tetragonal zirconia polycrystal
TZ-3Y	3Y ₂ O ₃ -ZrO ₂
TZ-8Y	8Y ₂ O ₃ -ZrO ₂
TZ-3Y/TZ-8Y layers	3Y ₂ O ₃ -ZrO ₂ - 8Y ₂ O ₃ -ZrO ₂ - layers
PMMA	Polymethylmethacrylate
SEM	Scanning electron microscope
EDX	Electron diffraction X-ray
XRD	X-Ray diffraction
CTE	Coefficient of thermal expansion
E _o	Electric field
F _g	Gravity
F _E	Electric field strength
F _T	Total Force

8 References

1. Besra, L. and M. Liu, *A review on fundamentals and applications of electrophoretic deposition (EPD)*. Progress in Materials Science, 2007. **52**(1): p. 1-61.
2. Boccaccini, A.R., I. Corni, and M.P. Ryan, *Electrophoretic deposition: From traditional ceramics to nanotechnology*. Journal of the European Ceramic Society, 2008. **28**(7): p. 1353-1367.
3. Boccaccini, A.R., et al., *Electrophoretic deposition of biomaterials*. Journal of the Royal Society Interface, 2010. **7**: p. S581-S613.
4. Vallet-Regi, M., *Evolution of bioceramics within the field of biomaterials*. Comptes Rendus Chimie, 2010. **13**(1-2): p. 174-185.
5. Salinas, A.J. and M. Vallet-Regi, *Evolution of ceramics with medical applications*. Zeitschrift Fur Anorganische Und Allgemeine Chemie, 2007. **633**(11-12): p. 1762-1773.
6. Hench, L.L., *Bioceramics - from Concept to Clinic*. American Ceramic Society Bulletin, 1993. **72**(4): p. 93-98.
7. Hench, L.L. and J. Badeni, eds. *An introduction to bioceramics*. 1993, World Scientific: Singapore.
8. Eichner, K. and H. Kappert, *Zahnärztliche Werkstoffe und ihre Verarbeitung*. Vol. 1. 2000. 326-372.
9. Holand, W., et al., *Bioceramics and their application for dental restoration*. Advances in Applied Ceramics, 2009. **108**(6): p. 373-380.
10. Conrad, H.J., W.J. Seong, and G.J. Pesun, *Current ceramic materials and systems with clinical recommendations: A systematic review*. Journal of Prosthetic Dentistry, 2007. **98**(5): p. 389-404.
11. Moldovan, O., et al., *Three-dimensional fit of CAD/CAM-made zirconia copings*. Dental Materials, 2011. **27**(12): p. 1273-1278.
12. Vafiadis, D. and G. Goldstein, *Single Visit Fabrication of a Porcelain Laminate Veneer with Cad/Cam Technology: A Clinical Report*. Journal of Prosthetic Dentistry, 2011. **106**(2): p. 71-73.

13. Oetzel, C. and R. Clasen, *Preparation of zirconia dental crowns via electrophoretic deposition*. Journal of Materials Science, 2006. **41**(24): p. 8130-8137.
14. Denry, I. and J.R. Kelly, *State of the art of zirconia for dental applications*. Dental Materials, 2008. **24**(3): p. 299-307.
15. Chevalier, J., et al., *The Tetragonal-Monoclinic Transformation in Zirconia: Lessons Learned and Future Trends*. Journal of the American Ceramic Society, 2009. **92**(9): p. 1901-1920.
16. Mochales, C., et al., *Monoclinic phase transformations of zirconia-based dental prostheses, induced by clinically practised surface manipulations*. Acta Biomaterialia, 2011. **7**(7): p. 2994-3002.
17. Piconi, C. and G. Maccauro, *Zirconia as a ceramic biomaterial*. Biomaterials, 1999. **20**(1): p. 1-25.
18. Garvie, R.C. and Nicholson, P.S., *Structure and Thermomechanical Properties of Partially Stabilized Zirconia in Cao-Zro2 System*. Journal of the American Ceramic Society, 1972. **55**(3): p. 152-&.
19. Bocanegra-Bernal, M.H. and S.D. De la Torre, *Phase transitions in zirconium dioxide and related materials for high performance engineering ceramics*. Journal of Materials Science, 2002. **37**(23): p. 4947-4971.
20. Manicone, P.F., P.R. Iommetti, and L. Raffaelli, *An overview of zirconia ceramics: Basic properties and clinical applications*. Journal of Dentistry, 2007. **35**(11): p. 819-826.
21. Silva, N.R.F.A., et al., *Modified Y-TZP Core Design Improves All-ceramic Crown Reliability*. Journal of Dental Research, 2011. **90**(1): p. 104-108.
22. Rieger, W., S. Köbel, and W. Weber, *Processing and Properties of Zirconia Ceramics for Dental Applications*. Spectrum Dialogue, 2008.
23. Andreiotelli, M., H.J. Wenz, and R.J. Kohal, *Are ceramic implants a viable alternative to titanium implants? A systematic literature review*. Clinical Oral Implants Research, 2009. **20**: p. 32-47.
24. Swab, J.J., *Low-Temperature Degradation of Y-Tzp Materials*. Journal of Materials Science, 1991. **26**(24): p. 6706-6714.
25. Pfaff, H.G., *Herstellung von Keramikkomponenten für die Endoprothetik, Die Keramikpaarung BIOLOX in der Hüftendoprothetik*. 1.CERASIV Symposium Stuttgart 1996, 1996.

26. Bocanegra-Bernal, M.H., *Hot Isostatic Pressing (HIP) technology and its applications to metals and ceramics*. Journal of Materials Science, 2004. **39**(21): p. 6399-6420.
27. Bousack, H., *Hot isostatic pressing (HIP): Techniques, applications and economical use*. Spez. Berichte der Kernforschungsanlage Jülich, 1985: p. 3.
28. Bocanegra-Bernal, M.H., et al., *Hot isostatic pressing (HIP) of alpha-Al(2)O(3) submicron ceramics pressureless sintered at different temperatures: Improvement in mechanical properties for use in total hip arthroplasty (THA)*. International Journal of Refractory Metals & Hard Materials, 2009. **27**(5): p. 900-906.
29. Guazzato, M., et al., *Strength, fracture toughness and microstructure of a selection of all-ceramic materials. Part II. Zirconia-based dental ceramics*. Dental Materials, 2004. **20**(5): p. 449-456.
30. Gobert, B., *Wol-Ceram®*. Quintessenz Zahntechnik, 2005. **31**(2): p. 152-162.
31. WOL-CERAM®, http://wolceram.de/cms/front_content.php?idcat=3, Editor, WOL-Dent GmbH: Bad Sobernheim.
32. WOL-CERAM®, <http://wolceram.de/cms/upload/bilder/herstellung/bruecken3.jpg>, Wol-DENT GmbH: Bad Sobernheim.
33. Boccaccini, A.R. and I. Zhitomirsky, *Application of electrophoretic and electrolytic deposition techniques in ceramics processing*. Current Opinion in Solid State & Materials Science, 2002. **6**(3): p. 251-260.
34. Corni, I., M.P. Ryan, and A.R. Boccaccini, *Electrophoretic deposition: From traditional ceramics to nanotechnology*. Journal of the European Ceramic Society, 2008. **28**(7): p. 1353-1367.
35. Ferrari, B. and R. Moreno, *EPD kinetics: A review*. Journal of the European Ceramic Society, 2010. **30**(5): p. 1069-1078.
36. Anne, G., et al., *Electrophoretic deposition as a novel near net shaping technique for functionally graded biomaterials*. Electrophoretic Deposition: Fundamentals and Applications li, 2006. **314**: p. 213-218.
37. Moritz, T., W. Eiselt, and K. Moritz, *Electrophoretic deposition applied to ceramic dental crowns and bridges*. Journal of Materials Science, 2006. **41**(24): p. 8123-8129.
38. Chlup, Z., H. Hadraba, and . *Alumina and Zirconia Based Layered Composites: Part 2 Fracture Response*. Key Engineering Materials, 2009. **412**: p. 227-232.

39. Hadraba, H., K. Maca, and Z. Chlup, *Alumina and Zirconia Based Composites: Part 1 Preparation*. Key Engineering Materials, 2009. **412**: p. 221-226.
40. Gong, J.H., H.Z. Miao, and Z.J. Peng, *Analysis of the nanoindentation data measured with a Berkovich indenter for brittle materials: effect of the residual contact stress*. Acta Materialia, 2004. **52**(3): p. 785-793.
41. Oliver, W.C. and G.M. Pharr, *An Improved Technique for Determining Hardness and Elastic-Modulus Using Load and Displacement Sensing Indentation Experiments*. Journal of Materials Research, 1992. **7**(6): p. 1564-1583.
42. Sato, N., et al., *Effect of particle size reduction on crack formation in electrophoretically deposited YBCO films*. Physica C, 2001. **357**: p. 1019-1022.
43. Kruger, H.G., et al., *Composite ceramic-metal coatings by means of combined electrophoretic deposition and galvanic methods*. Journal of Materials Science, 2004. **39**(3): p. 839-844.
44. Moritz, K. and T. Moritz, *ZrO₂ ceramics with aligned pore structure by EPD and their characterisation by X-ray computed tomography*. Journal of the European Ceramic Society, 2010. **30**(5): p. 1203-1209.
45. Moreno, R., B. Ferrari, and A.J. Sanchez-Herencia, *Electrophoretic forming of Al₂O₃/Y-TZP layered ceramics from aqueous suspensions*. Materials Research Bulletin, 1998. **33**(3): p. 487-499.
46. Ferrari, B., A.J. Sanchez-Herencia, and R. Moreno, *Aqueous electrophoretic deposition of Al₂O₃/ZrO₂ layered ceramics*. Materials Letters, 1998. **35**(5-6): p. 370-374.
47. Sharma, R., et al., *Diamond like carbon films as a protective surface on PMMA for biomedical applications*. Surface & Coatings Technology, 2010. **205**(7): p. 2495-2502.
48. Bermejo, R., et al., *Processing optimisation and fracture behaviour of layered ceramic composites with highly compressive layers*. Composites Science and Technology, 2007. **67**(9): p. 1930-1938.
49. Liang, Z. and S. Blackburn, *Analysis of crack development during processing of laminated ceramic tubes*. Journal of Materials Science, 2002. **37**(19): p. 4227-4233.
50. Zhang, Z.T., Y. Huang, and Z.Z. Jiang, *Electrophoretic deposition forming of SiC-TZP composites in a nonaqueous sol media*. Journal of the American Ceramic Society, 1994. **77**(7): p. 1946-1949.

51. Munz, D. and T. Fett, *Mechanisches Verhalten keramischer Werkstoffe*. 1989: Springer Verlag Berlin.
52. Thair, L., et al., *Development of apatite coatings on Ti-6Al-7Nb dental implants by biomimetic process and EPD: in vivo studies*. *Surface Engineering*, 2011. **27**(1): p. 11-18.
53. Chan, H.M., *Layered ceramics: Processing and mechanical behavior*. *Annual Review of Materials Science*, 1997. **27**: p. 249-282.
54. Fratzl, P., et al., *Hindered crack propagation in materials with periodically varying Young's modulus - Lessons from biological materials*. *Advanced Materials*, 2007. **19**(18): p. 2657-+.
55. Ma, J., et al., *Effect of porous interlayers on crack deflection in ceramic laminates*. *Journal of the European Ceramic Society*, 2004. **24**(5): p. 825-831.
56. Davis, J.B., et al., *Fabrication and crack deflection in ceramic laminates with porous interlayers*. *Journal of the American Ceramic Society*, 2000. **83**(10): p. 2369-2374.
57. Bueno, S. and C. Baudin, *Design and processing of a ceramic laminate with high toughness and strong interfaces*. *Composites Part a-Applied Science and Manufacturing*, 2009. **40**(2): p. 137-143.
58. Nahlik, L., et al., *Prediction of crack propagation in layered ceramics with strong interfaces*. *Engineering Fracture Mechanics*, 2010. **77**(11): p. 2192-2199.
59. Bermejo, R., et al., *Optimal strength and toughness of Al₂O₃-ZrO₂ laminates designed with external or internal compressive layers*. *Journal of the European Ceramic Society*, 2008. **28**(8): p. 1575-1583.
60. Jimenez-Pique, E., et al., *Hertzian contact fatigue on alumina/alumina-zirconia laminated composites*. *Journal of the European Ceramic Society*, 2005. **25**(15): p. 3393-3401.
61. Jimenez-Pique, E., et al., *Surface contact degradation of multilayer ceramics under cyclic subcritical loads and high number of cycles*. *International Journal of Refractory Metals & Hard Materials*, 2005. **23**(4-6): p. 375-381.
62. Sarkar, P., X.N. Huang, and P.S. Nicholson, *Zirconia-Alumina Functionally Graded Composites by Electrophoretic Deposition Techniques*. *Journal of the American Ceramic Society*, 1993. **76**(4): p. 1055-1056.

63. Sarkar, P., X.N. Huang, and P.S. Nicholson, *Structural ceramic microlaminates by electrophoretic deposition*. Journal of the American Ceramic Society, 1992. **75**(10): p. 2907-2909.
64. Nicholson, P.S., P. Sarkar, and X. Huang, *Electrophoretic Deposition and Its Use to Synthesize ZrO₂/Al₂O₃ Micro-Laminate Ceramic-Ceramic Composites*. Journal of Materials Science, 1993. **28**(23): p. 6274-6278.
65. Prakash, O., P. Sarkar, and P.S. Nicholson, *Crack Deflection in Ceramic/Ceramic Laminates with Strong Interfaces*. Journal of the American Ceramic Society, 1995. **78**(4): p. 1125-1127.
66. Hatton, B. and P.S. Nicholson, *Design and fracture of layered Al₂O₃/TZ3Y composites produced by electrophoretic deposition*. Journal of the American Ceramic Society, 2001. **84**(3): p. 571-576.
67. Hadraba, H., J. Klimes, and K. Maca, *Crack propagation in layered Al₂O₃/ZrO₂ composites prepared by electrophoretic deposition*. Journal of Materials Science, 2007. **42**(15): p. 6404-6411.
68. Llanes, L., et al., *Threshold strength evaluation on an Al₂O₃-ZrO₂ multilayered system*. Journal of the European Ceramic Society, 2007. **27**(2-3): p. 1443-1448.
69. Bermejo, R. and R. Danzer, *High failure resistance layered ceramics using crack bifurcation and interface delamination as reinforcement mechanisms*. Engineering Fracture Mechanics, 2010. **77**(11): p. 2126-2135.
70. de Portu, G., et al., *Abrasive wear in ceramic laminated composites*. Wear, 2006. **260**(9-10): p. 1104-1111.
71. Basu, B., N. Gupta, and P. Mallik, *Y-TZP ceramics with optimized toughness: new results*. Journal of Alloys and Compounds, 2004. **379**(1-2): p. 228-232.
72. Suci, C., et al., *Water-based tape-casting of SOFC composite 3YSZ/8YSZ electrolytes and ionic conductivity of their pellets*. Ceramics International, 2012. **38**(1): p. 357-365.
73. Chevalier, J., et al., *Critical effect of cubic phase on aging in 3 mol% yttria-stabilized zirconia ceramics for hip replacement prosthesis*. Biomaterials, 2004. **25**(24): p. 5539-5545.
74. Chevalier, J., *What future for zirconia as a biomaterial?* Biomaterials, 2006. **27**(4): p. 535-543.

75. Ferrari, B., et al., *Multilayer coatings with improved reliability produced by aqueous electrophoretic deposition*. Journal of the European Ceramic Society, 2006. **26**(1-2): p. 27-36.
76. Maca, K., H. Hadraba, and J. Cihlar, *Electrophoretic deposition of alumina and zirconia - I. Single-component systems*. Ceramics International, 2004. **30**(6): p. 843-852.
77. Put, S., J. Vleugels, and O. Van Der Biest, *Gradient profile prediction in functionally graded materials processed by electrophoretic deposition*. Acta Materialia, 2003. **51**(20): p. 6303-6317.
78. Sarkar, P., S. Datta, and P.S. Nicholson, *Functionally graded ceramic/ceramic and metal/ceramic composites by electrophoretic deposition*. Composites Part B-Engineering, 1997. **28**(1-2): p. 49-56.
79. Chen, C.Y., S.Y. Chen, and D.M. Liu, *Electrophoretic deposition forming of porous alumina membranes*. Acta Materialia, 1999. **47**(9): p. 2717-2726.
80. Put, S., et al., *Functionally graded ceramic and ceramic-metal composites shaped by electrophoretic deposition*. Colloids and Surfaces a-Physicochemical and Engineering Aspects, 2003. **222**(1-3): p. 223-232.
81. Tabellion, J. and R. Clasen, *Electrophoretic deposition from aqueous suspensions for near-shape manufacturing of advanced ceramics and glasses - applications*. Journal of Materials Science, 2004. **39**(3): p. 803-811.
82. Kaya, C., *Al₂O₃-Y-TZP/Al₂O₃ functionally graded composites of tubular shape from nano-sols using double-step electrophoretic deposition*. Journal of the European Ceramic Society, 2003. **23**(10): p. 1655-1660.

Acknowledgements

My thanks go to PD Dr. W.-D. Müller for the assignment of this work and the friendly support.

The present work is part of a project within the priority programme 1420 (<http://spp1420.mpikg.mpg.de/projects/hierarchy-of-microstructural-features-as-the-origin-of-fracture-resistance-in-dentine-and-ceramic-composites>) of the German Research Foundation (DFG), which is under the special direction of Prof. Claudia Fleck from the Technical University of Berlin. The financial support by the DFG is greatly appreciated, as well as the guidance of Prof. Fleck.

Special thanks go to Dr. Carolina Mochales Palau for her big support. Her advice and the dialogue with her were a big help and much appreciated.

Moreover I would like to thank Nikolaos Kachrimanis, who made the time much more pleasant and enjoyable.

At last I thank my family for their support and encouragement without which this work would not have been possible.

Publications

Posters/Abstracts

DKG-Jahrestagung: 28. März - 30. März 2011, Saarbrücken

Electrophoretic deposition of Y-TZP for medical applications

18. Symposium Verbundwerkstoffe und Werkstoffverbunde: 30. März - 01. April 2011, Chemnitz

Ceramic EPD on polymers

DGBM-Jahrestagung: 10. November - 12. November 2011, Gießen

Crack propagation in EPD yttria-stabilized zirconia ceramics

DGBM-Jahrestagung: 1. November - 3. November 2012, Hamburg

Tetragonal-cubic zirconia multilayered EPD constructs: crack development

DENTSPLY Förderpreis 2012: 9. November 2012

Elektrophoretische Abscheidung von Keramik-Partikeln

Erklärung

„Ich, Christine Fleckenstein, erkläre, dass ich die vorgelegte Dissertation mit dem Thema: „Electrophoretic Deposition (EPD) of Ceramics: A potential technique to improve mechanical properties in dental appliances“ selbst verfasst und keine anderen als die angegebenen Quellen und Hilfsmittel benutzt, ohne die (unzulässige) Hilfe Dritter verfasst und auch in Teilen keine Kopien anderer Arbeiten dargestellt habe.“

7. November 2012

Christine Fleckenstein

Lebenslauf

Mein Lebenslauf wird aus datenschutzrechtlichen Gründen in der elektronischen Version meiner Arbeit nicht veröffentlicht.

