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# Mixed zirconia calcium phosphate coatings for dental implants: Tailoring coating stability and bioactivity potential ☆

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ABSTRACT

Enhanced coating stability and adhesion are essential for long-term success of orthopedic and dental implants. In this study, the effect of coating composition on mechanical, physico-chemical and biological properties of coated zirconia specimens is investigated. Zirconia discs and dental screw implants are coated using the wet powder spraying (WPS) technique. The coatings are obtained by mixing yttria-stabilized zirconia (TZ) and hydroxyapatite (HA) in various ratios while a pure HA coating served as reference material. Scanning electron microscopy (SEM) and optical profilometer analysis confirm a similar coating morphology and roughness for all studied coatings, whereas the coating stability can be tailored with composition and is probed by insertion and dissections experiments in bovine bone with coated zirconia screw implants. An increasing content of calcium phosphate (CP) resulted in a decrease of mechanical and chemical stability, while the bioactivity increased in simulated body fluid (SBF). In vitro experiments with human osteoblast cells (HOB) revealed that the cells grew well on all samples but are affected by dissolution behavior of the studied coatings. This work demonstrates the overall good mechanical strength, the excellent interfacial bonding and the bioactivity potential of coatings with higher TZ contents, which provide a highly interesting coating for dental implants.



## 1. Introduction

Dental implants undergo several load-bearing conditions, such as chewing pressure, and thus require high mechanical reliability. They must be able to withstand both, peak loads and millions of low level cyclic stresses occurring during lifetime while chewing [1]. This can be achieved by the use of metallic materials; the vast majority of dental implants currently used are made of titanium or titanium alloy. Both materials have been established for years and are characterized by a high degree of biocompatibility, favorable mechanical properties and low corrosion rates [2]. Nevertheless, several reports about questionable biostability have been stated [3,4].

Ceramics, usually yttria-stabilized zirconia (TZ), receive increased attention as dental materials due to their low toxicity and beneficial mechanical properties like high fracture toughness and bending strength as well as satisfying esthetic requirements. Despite of the biocompatible properties, TZ is known to be bioinert and thereby no stimulation of bone ongrowth is achieved [5–7]. As a result, fibrous layer may form around the implant and induce aseptic loosening [4,8]. Besides surface roughness inorganic coatings on the material surface have been proposed in literature to overcome the instability and promote direct attachment to bone tissue [9,10]. Calcium phosphate (CP) based materials, such as hydroxyapatite (HA) and tricalcium phosphate (TCP) are considered to be bioactive and thus stimulate bone regeneration [11]. However, pure CP coatings exhibit a poor stability and provide a weak bonding strength to the substrate [12–15]. Therefore, one challenge is to control the adhesion strength of the coating together with a good bioactivity but without affecting the bulk properties of the substrate, so that long-term stability can be achieved.

To overcome these drawbacks of pure CP coatings several studies used TZ reinforced HA coatings on titanium to combine enhanced mechanical properties with an increased osseointegration. The addition of TZ to HA and subsequent sintering provides an enhanced coating stability as well as better coating–substrate adhesion caused by improved particle-substrate interactions when applied on zirconia substrates [16–18]. Sintering, a thermally driven process, gives the opportunity for diffusion processes between the particles of coating and substrate, which in turn may have a great influence on the adhesion [19].

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Both, bone-implant bond strength and coating-implant bond strength, are two important factors for successful and strong anchorage of the implant to bone tissue [20]. Thus, a poor stability within the coating and a weak bonding of the coating to the substrate could cause failure or delamination due to the occurring forces during insertion and after implantation [21,22]. Therefore, coating composition and the coating characteristics involved are of great interest to achieve a high effectiveness and long-term stability of the implant.

Regarding the significance of coating stability and adhesion the aim of this study was to assess the effect of coating composition on mechanical, physico-chemical and biological properties of coated zirconia specimens. Different mixed coatings consisting of TZ and CP were prepared by wet powder spraying (WPS) and subsequently investigated for microstructure, phase analysis, coating adhesion and mechanical strength. In vitro dissolution behavior, and surface morphology in simulated body fluid (SBF) as well as proliferation and differentiation of human osteoblasts (HOB) were examined to understand and evaluate the mechanical and chemical stability, and bioactivity of different coating compositions.

## 2. Materials and methods

### 2.1. Coating preparation

The details of substrate and suspension preparation, as well as the coating process are described in Pardun et al. [18].

Briefly, zirconia discs (diameter (Ø) = 15 mm, height (h) = 1.7 mm) were fabricated using commercially available TZ-3YSB-E powder (Tosoh, Tokyo, Japan) and uniaxially pressed at 38 MPa. After pressing, the substrates were isostatically densified at 1200 bar for 5 min and pre-sintered at 1100 °C for 2 h. Dental implants (length (l) = 17 mm, Ø = 4.5 mm) prepared from a zirconia feedstock (INMAFEED K1012, INMATEC Technologies GmbH, Rheinbach, Germany) were fabricated via injection molding and subsequently pre-sintered at 950 °C for 2 h (Fraunhofer IFAM, Bremen, Germany).

The different mixed suspensions for coating were prepared of HA (Sigma-Aldrich Chemie GmbH, Munich, Germany) and TZ-3YS-E powder (TZ, Tosoh, Tokyo, Japan), coating compositions are shown in Table 1. The aqueous ceramic suspensions consisted of different amounts of HA and TZ and were stabilized with polyacrylic acid-based dispersant (PAA, 12 mg/g ceramic powder, Syntran® 8220, Interpolymer GmbH, Hassloch, Germany) and at pH 10 by the addition of ammonium hydroxide solution (25% $NH_3$ basis, Sigma-Aldrich). As reference material a pure HA coating was used. All suspensions were homogenized by ultrasonication (Sonifier 450, Branson, Dietzenbach, Germany) for 10 min (mixed coatings) and 3 min (pure HA coating).

The coating of pre-sintered substrates was done with WPS. The substrates were fixed and coated using a double-action airbrush spray gun (BD 183-K, Artistic Life, Boenen, Germany) with a working distance of 200 mm. Coating deposition was performed with an air pressure of 2 bar, a relative humidity of ~60% and an airbrush nozzle with Ø 0.8 mm. After coating the samples were dried for 24 h at room temperature and afterwards sintered at 1500 °C for 2 h. All subsequent characterizations were performed on sintered samples.

**Table 1**
Coating composition of the different mixed coatings.

| Sample name | TZ | | HA | |
|---|---|---|---|---|
| | wt.% | vol.% | wt.% | vol.% |
| CP | – | – | 26.9 | 12.0 |
| TZCP 1:2 | 12.9 | 3.0 | 26.9 | 12 |
| TZCP 1:1 | 21.1 | 5.1 | 21.1 | 9.9 |
| TZCP 2:1 | 29.5 | 7.5 | 15.4 | 7.5 |

### 2.2. Coating characterization

The surface morphology of the coatings was analyzed using a scanning electron microscopy (SEM, Camscan Series 2, Obducat CamScan Ltd., Cambridgeshire, United Kingdom) at 20 kV operating in secondary electron mode and previously sputter coated with gold for 60 s (K550, Emitech, West Sussex, UK).

Measurements of the surface roughness were characterized with an optical profilometer (Plμ2300, Sensofar, Terassa, Spain). Areas of 477 × 636 $\mu m^2$ were scanned and the average surface roughness was calculated according to ISO 25178.

Crystal phase analysis was carried out by grazing incidence X-ray diffraction (GI-XRD) using an Ultima IV type III diffractometer (Rigaku, Tokyo, Japan) equipped with Cross Beam Optics (CBO) and Cu Kα radiation. Each run was performed with 2 theta (2θ) values between 20° and 70° carried out in parallel beam mode with a fixed incident angle of 0.5°.

### 2.3. Characterization of mechanical properties

Coating adhesion was determined with scratch tests performed by a pencil hardness tester (PH-5800, BYK-Gardner GmbH, Geretsried, Germany) according to ISO 15184. The mechanical adhesion between substrate and coating was qualitatively examined with a pencil (Vickers hardness 90.6 ± 2.5 HV 0.2) and a pencil-shaped bovine femur (Vickers hardness 89.8 ± 5.2 HV 0.2), which were fixed in a sclerometer and moved over the surface with a constant load of 7.5 N and a velocity of 1 mm/s along a 12 mm track. Prior to SEM investigation graphite and bone leftovers on the sample surface were burned out at 1000 °C and 1400 °C, respectively.

Biaxial flexural strengths of the coated specimens (Ø = 15 mm, h = 1.7 mm) were tested with the ball on three balls (B3B) test using a universal testing machine (Zwick/Roell Z005, Ulm, Germany) with a constant speed of 0.5 mm/min and metal balls of 4 mm radius. The flexural strength was calculated applying the following equation [23]:

$$\sigma\max = \frac{3\cdot F\cdot(1+\nu)}{4\cdot\pi\cdot t^2}\cdot\left[1+2\ln\left(\frac{Ra}{t/3}\right)+\frac{1-\nu}{1+\nu}\cdot\left(1-\frac{(t/3)^2}{2\cdot Ra}\right)\cdot\left(\frac{Ra}{R}\right)^2\right] \quad (1)$$

where: F is the applied load, $\nu$ the Poisson's ratio of the substrate material (here 0.32 for TZ), t the sample thickness, Ra the support radius and R the sample radius. The strength was tested on 30 samples for each coating. Furthermore, fracture surfaces of the B3B specimens were observed under SEM to analyze the coating–substrate interface.

### 2.4. Insertion and dissection of coated zirconia dental implants in bovine rip bone

The surface coated zirconia screws (n = 10) were inserted into predrilled holes of five fresh bovine rip bones. The insertion was carried out with drilling and insertion tools from the similarly macrodesigned implant system (BEGO Semados® RI; BEGO Implant Systems, Bremen, Germany) and performed according to the clinically approved protocols provided by the manufacturer.

After careful dissection of the implants SEM was used to assess coating morphology and stability. To further examine the coating stability at the thread tips, the same samples were embedded in resin (EpoFix, Struers GmbH, Willich, Germany), grounded to the middle of the implant and examined by SEM.

### 2.5. Dissolution behavior

To test the dissolution behavior of the various coatings, specimens were placed into sterile polystyrene culturing dishes (24-well