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Development of thin electrophoretically deposited hydroxyapatite layers on TiAl6V4 hip prosthesis

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Abstract Hydroxyapatite ceramics for biomedical applications are often used in form of coatings to increase the biocompatibility of metallic implants, e.g. the femoral shaft of a hip prosthesis. A new method to produce such layers is electrophoretic deposition (EPD). The aim of this study was to investigate the influence of different powders and process parameters on the quality of the electrophoretically deposited thin HA layers. In order to attain layers with a thickness less than 50 μm, it is essential to use fine powders with particle sizes in the sub-micron range, and to stabilize these powders in suspension. We show that commercially available hydroxyapatite powders, which usually have a strong tendency to agglomerate, can be milled to particle sizes smaller than 500 nm by adding an organic dispersant. When such milled powders are used together with optimized process parameters, thin and homogenous layers can be produced by EPD. Using either aqueous or non-aqueous suspensions, hydroxyapatite layers can be deposited directly onto a metallic hip shaft, or onto a polymeric membrane, producing thin free-standing ceramics used for special biomedical applications.

Introduction

Over the last 40 years, many studies have been conducted with the aim to improve the fixation of metallic implants in human bone. One way to improve implant fixation is to structure the surface, e.g. through grit blasting. Another strategy is to enhance the biocompatibility of the surface, e.g. by depositing a calcium-phosphate (CaP) layer. These CaP-materials possess adjustable resorption properties and an excellent biocompatibility because of their similarity to the human bone. Since the publication of first clinical results by Furlong and Osborn [1], many studies have shown improved fixation and long-term stability of HA coated metallic implants [2–5]. However, in spite of the well-known advantages that these coated implants are known to have, their use is still controversially discussed [6]. CaP-coatings are currently deposited on metallic implants by plasma spraying. Most of the problems that have been associated with HA coated implants are caused by this deposition method. Due to the high temperatures that occur during the plasma spraying process, the resulting coatings do not have an exactly defined phase composition [7]. Additionally, layers produced by this method have a rather high thickness, resulting in insufficient adhesion strength [8]. Experiences from the last decades show that the use of thin HA layers with a defined phase composition can be a solution for the above-mentioned problems. These layers preserve the roughness of the structured metallic shaft and offer enhanced adhesion strength. Therefore, there is a need for thin HA coatings on hip prosthesis that possess high adhesion strength, defined phase composition and good reproducibility. An new method to produce these layers may be electrophoretic deposition (EPD). With this technique, thin layers with enhanced adhesion strength can be produced.

In the last few years some work has been carried out in the field of EPD of powders for biomedical

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applications, especially hydroxyapatite. Sub-micron HA powders with various morphologies and particle sizes were produced by Wei et al., and the influence of these parameters on the homogeneity of coatings on Ti6Al4V metal substrates produced via EPD was investigated [9]. The use of sub-micron powders allows to produce thin layers of HA by EPD and to reduce the sintering temperature. This is important since when the temperature exceeds above 1,000 °C, interfacial reactions and decomposition of the hydroxyapatite can take place [10, 11]. The influence of different parameters, like deposition time or voltage applied, on the amount of HA powder deposited in the EPD process was studied by Zhitomirsky and Gal-Or [12]. Especially nature, amount and processing of addition of organic additives (dispersing agents and/or binders) are crucial factors for the viscosity of a slurry, and consequently, its homogeneity, determining the mechanical properties of the deposited layer [13].

In one of the few papers dealing with the deposition of hydroxyapatite powders on metallic substrates, the authors mainly concentrate on attaining layers in a very short time. To accomplish this, they recommend the use of high voltages (up to 800 V) over a few seconds [14].

The principle aim of our study was to show the feasibility of using EPD to produce a biocompatible HA layer, either as a free-standing thin ceramic or as a thin layer on a hip endoprosthesis shaft. An essential requirement is the use of a sub-micron powder. Therefore, commercially available HA powders were milled to attain sub-micron particle size and stabilized against reagglomeration. The optimal combination of additives and EPD parameters for the successful deposition of these sub-micron powders were ascertained. An aqueous suspension and membrane-method EPD were used to produce thin ceramics. The possibility to redispers the milled powder in alcohol without agglomeration enables the EPD of a thin HA layer on a TiAl6V4 hip shaft.

Materials and methods

Materials and characterization

Two different commercially available hydroxyapatite powders (''B'' and ''M'') were used for the milling experiments. Before and after milling, the powders were characterized by scanning electron microscopy (SEM) (FEI Quanta 200, Germany), X-ray diffraction (XRD) (Seiffert 3000, Germany) and particle size measurements (CILAS 1064L, France).

Milling

Milling was done with a planetary ball mill (Retsch PM 400, Germany) using water as milling media and corundum crucible and balls. Different parameters like milling time, diameter of the milling balls, powder-to-balls-ratio or the use of particle stabilizing additives were varied to find the optimal milling conditions.

Electrophoretic deposition

For the EPD we chose the milled powder B that had a mean particle size in the sub-micron range (see Table 1).

Aqueous EPD (membrane-method)

A water-based slurry with under 5 wt.% powder content and with 2 wt.% (relating to the powder) citric acid as dispersant was prepared and used in an electrophoresis cell for the deposition of an HA layer on a cellophane membrane (Fig. 1). Parameters like current and voltage, deposition time or powder content of the slurry were varied and optimized with the aim to get a thin homogeneous HA layer. The fracture surfaces of the green bodies were examined by SEM in low-vacuum mode (without a conducting layer). The ceramic layer was removed from the membrane and sintered at 1,300 °C in air atmosphere. Both the as fired and the fractured surface of the sintered ceramics were analyzed by conventional SEM to examine the homogeneity of the layer.

Non-aqueous EPD (conventional technique)

For conventional EPD, a slurry consisting of 58 wt.% of the milled powder B in alcohol (p.a. quality) with 2 wt.% citric acid as a dispersant was prepared. A carbon coated beaker and a TiAl6V4 hip shaft were used as electrodes. Parameters of the electrophoretical deposition were optimized to make the layer as thin as possible. After drying, the coated hip shaft was heated up to 500 °C in air atmosphere in a conventional furnace (Nabertherm, Germany) with a dwell time of 1 h.

Table 1 Particle size distribution of commercially available powders before and after milling with optimized parameters

Powder	d_{10} (μm)	d_{50} (μm)	d_{90} (μm)
B	1.33	5.63	18.07
B milled	0.22	0.57	1.16
M	1.7	5.05	13.2
M milled	0.14	0.3	0.56

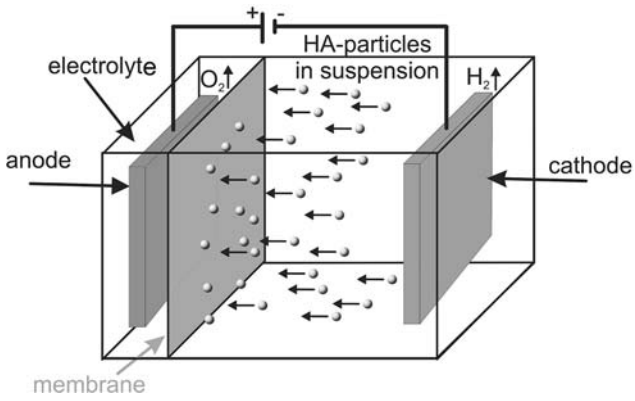

Fig. 1 Schematic drawing of the electrophoreses cell for the membrane-method

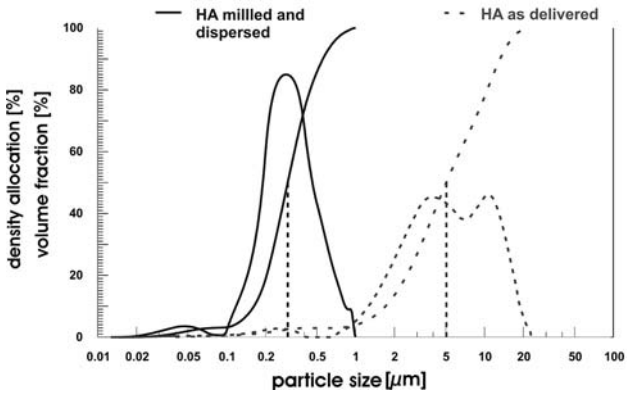

Fig. 2 Particle size distribution of the milled, dried and redispersed powder B

Results and discussion

Milling

The results of the milling experiments are summarized in Tables 1 and 2.

Before milling, the powders B and M had similar particle size distributions with a mean particle size (d_{50}) of approx. 5 µm (Table 1 and Fig. 2). After milling, the mean particle size decreased significantly to 0.57 µm for powder B and 0.3 µm for powder M, and the d_{90}–value was lowered to 1.16 µm and 0.56 µm, respectively.

Figure 2 shows the particle size distribution of powder B after milling for 17 h. When using citric acid as dispersant during milling, the powders could even be dried without agglomeration (see Fig. 3) and subsequently be redispersed, using water or alcohol.

The mean particle size (d_{50}) decreased with increasing milling time, and was lower when using a mixture of 5 and 10 mm balls. The addition of an organic acid was essential to stabilize the milled HA particles against reagglomeration. Citric acid gave the best results (Table 2).

The resulting mean particle size is in the same range as those measured by Rodriguez-Lorenzo et al. [15] after a milling time of 20 h. But compared to their results, the addition of citric acid prevented the particles from reagglomeration and the d_{90}–value of our milled powders is significantly lower.

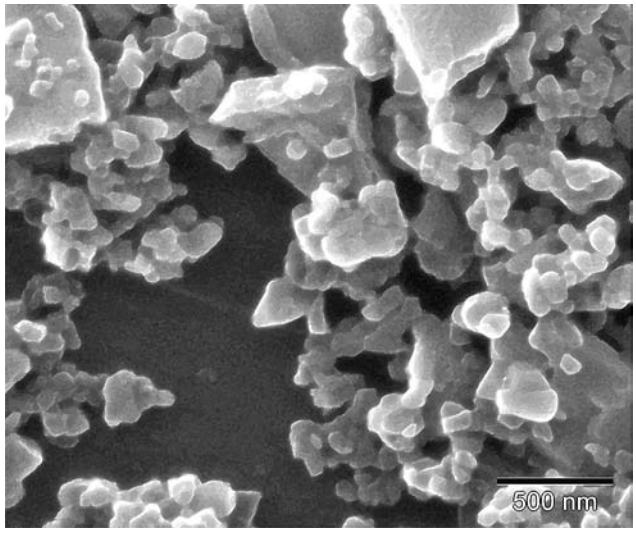

Fig. 3 SEM image of powder B after 17 h milling and drying

In examining the milled powders with XRD, only the typical peaks of hydroxyapatite (ICDD 09-0432)

Table 2 Influence of different parameters on the mean particle size d_{50} of HA powders

Powder	Milling time (h)	Additive	Diameter of balls (mm)	d_{50} (µm)
(a) Influence of the diameter of the milling balls on the mean particle size d_{50} of HA powder M				
M	6.5	Organic acid	5	1.44
M	6.5	Organic acid	5 + 10	0.48
(b) Influence of milling time on the mean particle size d_{50} of HA powder M				
M	6.5	Organic acid	5 + 10	0.48
M	29	Organic acid	5 + 10	0.3
(c) Influence of additives on the mean particle size d_{50} of HA powder B				
B	17	Inorganic acid	5 + 10	0.87
B	17	Organic acid	5 + 10	0.57

can be seen, and no significant amount of wear particles from corundum can be detected.

These findings show that commercially available hydroxyapatite powders can be milled to a sub-micron particle size distribution. Due to stabilization with citric acid, the milled powders can be used in both aqueous and alcoholic suspensions.

Electrophoretic deposition

Electrophoretic deposition of the un-milled powders B and M resulted in thin layers with cracks or in layers with a thickness of >100 μm. Therefore, a milled powder, in this case powder B, was used for the EPD experiments. Based on the results from testing various process parameters, the optimal electrophoresis parameters for achieving thin, homogeneous and dense layers of hydroxyapatite are summarized in Table 3. In both cases the addition of a binder was not necessary.

Aqueous EPD

Applying the parameters listed in Table 3, the EPD of the HA powder on the membrane resulted in green bodies with approx. 30 μm thickness and without detectable inhomogeneities even on the micrometer scale (Fig. 4). These layers were stable during handling.

Increasing the deposition time or the powder content of the slurry led to thicker layers which were not homogenous and cracked during drying. Choosing different current or voltage values than those listed in Table 3 also resulted in the formation of non-homogenous HA layers on the membrane.

The sintered HA layers are translucent. A shrinkage of the deposited layer of more than 30% in perpendicular direction to the membrane can be observed by comparing Figs. 4 and 5, the shrinkage in plane was not measured. The sintered layer is almost dense and there are only very few and small pores inside the layer (Fig. 5).

As can be seen on the surface of the deposited layer (inset in Fig. 4), the HA grains grew during sintering.

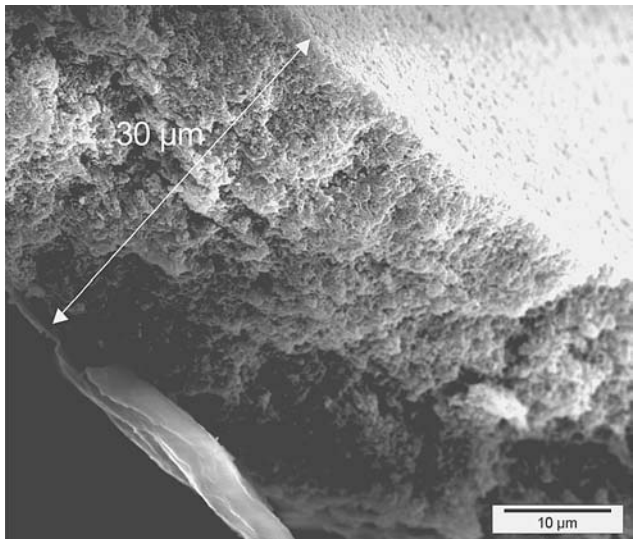

Fig. 4 SEM image of the deposited HA layer before sintering (cross section of the fracture surface)

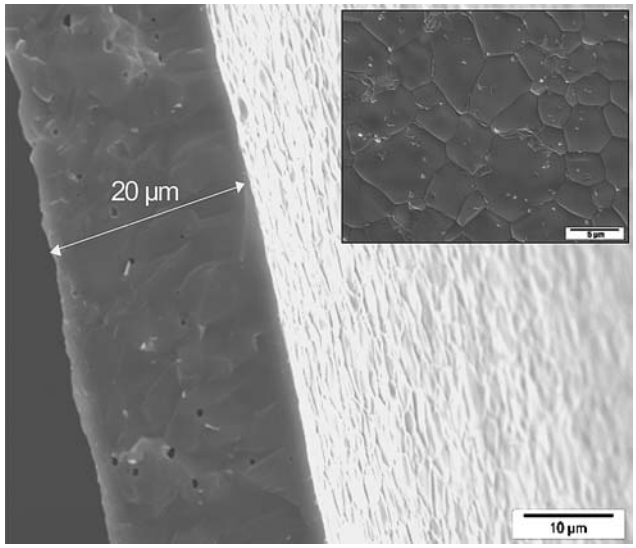

Fig. 5 SEM image of the same layer after sintering at 1,300°C (cross section) (inset: higher magnification of the surface)

Comparing the microstructures of the ceramics produced with the milled powders (d_{50}-value 0.57 μm) and ceramics produced with un-milled powders (d_{50}-value

Table 3 Optimized parameters for the electrophoretic deposition of a sub-micron HA powder

Medium	Substrate	Time	Current	Voltage	Additives	Powder content of the slurry
(a) Aqueous EPD						
Water	Membrane	700 s	0.5–1.3 A	10/20 V	2 wt.% citric acid	<5 wt.%
(b) Alcoholic EPD						
Ethanol	Metallic hip shaft	300 s	2 A	30 V	2 wt.% citric acid	58 wt.%

5.63 μm) by conventional methods, the grain size after sintering at 1,300 °C is in the same range. Thus, the use of the milled powders is essential for a successful EPD and to achieve thin ceramic layers, but the microstructure after sintering is not influenced.

Non-aqueous EPD

In Fig. 6a the HA coated part of the TiAl6V4 hip shaft is shown. The left part noted ''epd'' is the electrophoretically coated part.

When choosing a low voltage and a short deposition time, the EPD process resulted in a thin HA layer. This is in good accordance with the results of Xiu et al., who attained layers with a thickness of approx. 50 μm when applying 30 V over 1 min [16]. Even though this layer covers the surface of the TiAl6V4 shaft, the surface roughness is only slightly decrease compared to the original shaft (compare Fig. 6c, b). Because of the low calcination temperature (500 °C, to stay well below the temperature that is detrimental for the metal), the HA-particles could still be seen (Fig. 7).

Despite the low calcination temperature, the adhesion strength of the layer is good and the coated shaft could be handled without problems. The layer did not show any delamination or scratching marks afterwards.

The combination of using a sub-micron HA powder in a stable suspension and applying optimized parameters for the EPD of an HA layer on a TiAl6V4 hip shaft resulted in a thin, homogenous layer with good adhesion strength [16]. Because the surface roughness was not altered much due to the low thickness of the layer, biocompatibility and ingrowth of the TiAl6V4 shaft should be markedly increased [17].

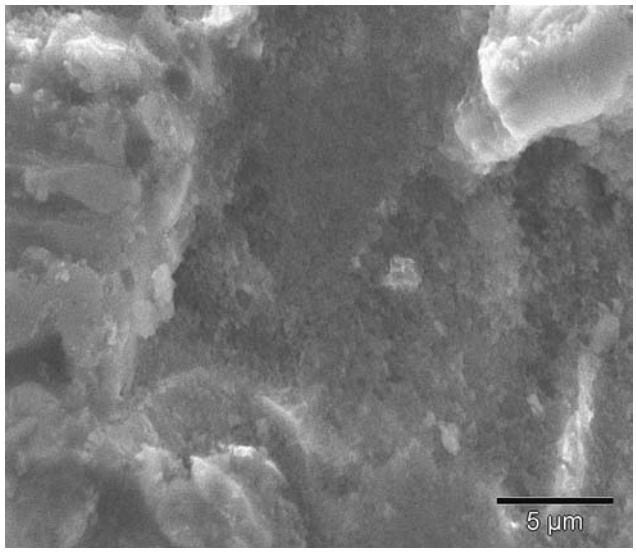

Fig 7 SEM image of the EPD coated part of the hip shaft at higher magnification (the preserved roughness and the uniform covering can be seen)

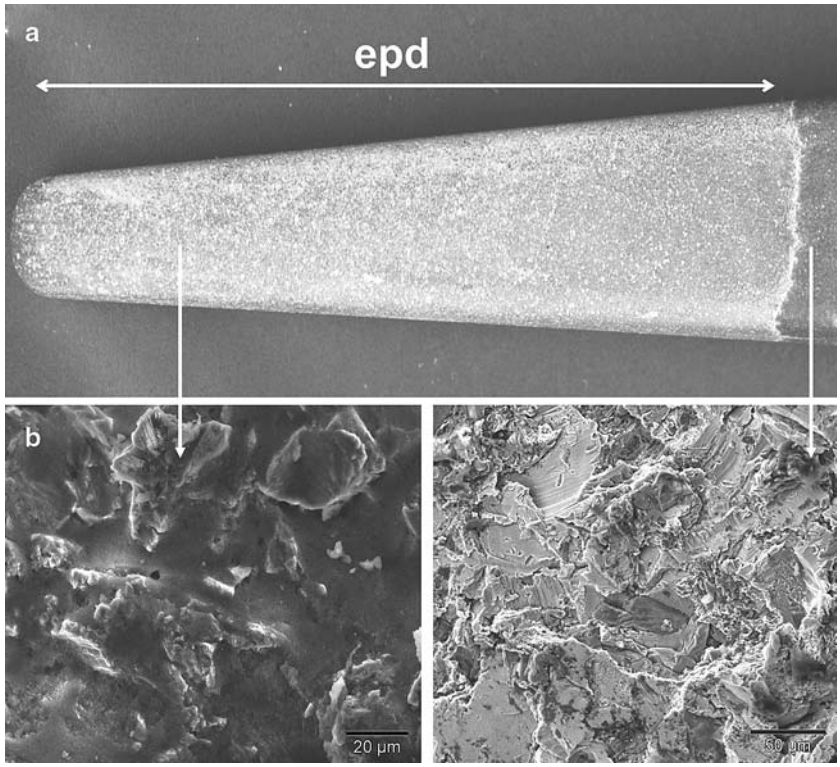

Fig. 6 Images of an HA coated hip shaft; (**a**) Photographic image of the shaft (''epd'' marks the electrophoretically coated part), (**b**) SEM image of the HA coated part, (**c**) SEM image of the uncoated part (surface)

Summary

We have shown in our study that thin HA layers can be produced by EPD either using the membrane-method to produce a thin, free-standing ceramic for special applications or conventional EPD to coat a metallic hip shaft. In order to be successful, it is essential that a sub-micron powder is used. Therefore, commercially available HA powders with a d_{50}-value of about 5 μm were milled to mean particle sizes in the sub-micron range (d_{50}-value 0.56–0.3 μm). The use of these powders, in combination with the optimization of the organic additives and the process parameters of the EPD, are crucial requirements for successful EPD of thin homogenous layers. The main goal of this study was to demonstrate that thin HA layers can be deposited on a TiAl6V4 hip prosthesis by optimizing materials and process parameters.

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