Deposition of calcium phosphate coatings with defined chemical properties using the electrostatic spray deposition technique

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Abstract

The electrostatic spray deposition (ESD) technique was used for biomedical purposes in order to deposit calcium phosphate (CaP) coatings onto titanium substrates. The relationship between various deposition parameters and the chemical properties of deposited coatings was investigated in order to be able to deposit CaP coatings with tailored chemical characteristics.

The results showed that the chemical properties of the coatings were determined by both physical, apparatus-related factors and chemical, solution-related parameters. By varying the processing parameters of the technique, several crystal phases and phase mixtures were obtained, ranging from carbonate-free phases such as meta- and pyrophosphates, monetite and various tricalcium phosphates to carbonate-containing phases such as various carbonate apatites and calcite. On the basis of these results, a chemical mechanism of coating formation was proposed. Essentially, the deposition of the various crystal phases was the result of an acid–base reaction between basic CO_3^{2-} groups (originating from solvent decomposition reactions) and acidic HPO_4^{2-} groups from an intermediate monetite ($CaHPO_4$) phase of the CaP precipitate. The amount of carbonate incorporation (ranging from 0 to 15 wt%) determined the crystal and molecular structure of the deposited coatings.
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1. Introduction

Because of its similarity to the inorganic component of bone and teeth, calcium phosphate (CaP) ceramics were early considered as a suitable class of biomaterials for biomedical purposes. CaP materials are categorized as bioactive ceramics, which implies that the implant material bonds to surrounding bone tissue, resulting in a strong interface between bone and the implant surface.[1] Generally, the degree of bioactivity of CaP ceramics is strongly related to the physico-chemical properties – and correspondingly to the synthesis conditions – of the implant material surface upon exposure to body fluid.[2,3] Due to their intrinsic brittleness, CaP ceramics are frequently used as a coating on metallic implants to improve their biological performance.[4] However, using conventional deposition methods like plasma-spraying

or sputter-deposition, coating properties (in terms of coating chemistry and morphology) can be varied only to a limited extent. This in contrast to the electrostatic spray deposition (ESD) technique, which enables deposition of inorganic thin films with a variety of chemical and morphological properties.[5,6]

Briefly, the basic principle of ESD is the generation of a spray of charged, micron-sized droplets. This is accomplished by means of electrostatic atomization[7] of precursor solutions that contain inorganic precursor salts. These spray droplets are subsequently attracted by the grounded and heated substrate as a result of the applied potential difference (typically between 5 and 10 kV). After complete solvent evaporation, a thin layer is left onto the substrate surface.

In a previous study, the feasibility of the ESD technique was proven for the production of thin calcium phosphate coatings.[8] In order to be able to deposit ESD-coatings with tailored chemical properties, we have investigated the influence of physical (apparatus-related) and chemical
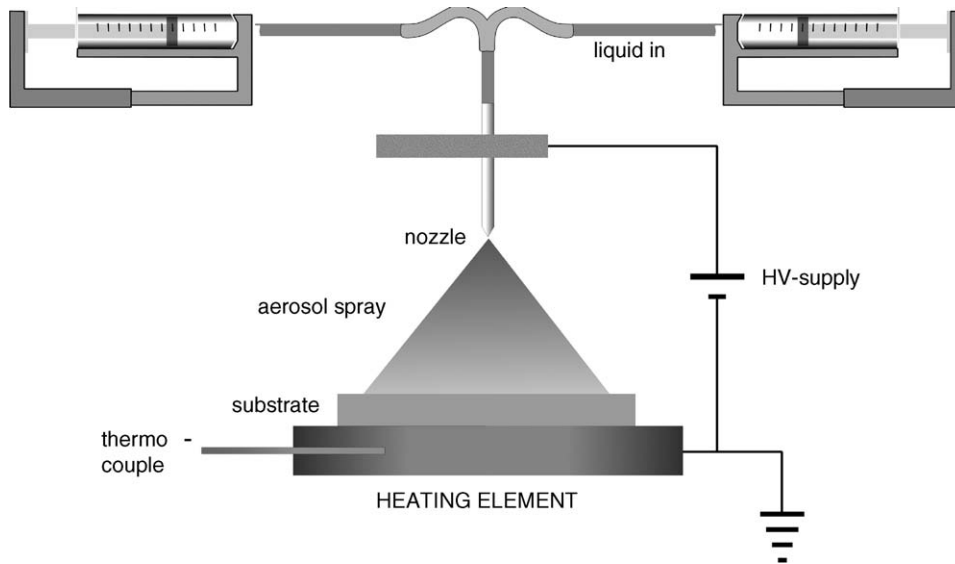
Fig. 1. Experimental set-up of the electrostatic spray deposition technique.

(solution-related) deposition parameters on the chemical properties of the deposited coatings.

2. Experimental

A commercially available ESD set-up (Advanced Surface Technology, Bleiswijk, The Netherlands) was used to deposit CaP coatings onto Ti-substrates. Fig. 1 gives a schematic view of the set-up. Precursor solutions containing Ca and P precursor salts were pumped towards a spraying nozzle by means of a syringe pump (Kd Scientific 220). Ca and P precursor solutions were prepared by dissolving calcium salts (either $Ca(NO_3)_2 \cdot 4H_2O$ or $CaCl_2 \cdot 2H_2O$) and phosphoric acid (H_3PO_4) in organic solvents (butyl carbitol ($C_8H_{18}O_3$) and/or ethanol). A two-component nozzle with separate inlet for Ca and P precursor solutions was used as standard nozzle (stainless steel, flat outlet, inner and outer outlet diameter of 0.9 and 1.4 mm, respectively) in order to avoid premature precipitation of precursor solutions prior to spray generation. This new nozzle geometry was compared with a conventional one-component nozzle geometry of the same dimensions using premixed precursor solutions (Fig. 2). Machined, commercially pure (cp) Ti-substrates (diameter 12 mm, 1.5 mm thickness) were used as substrate material for the deposition of the CaP coatings. The substrates were cleaned ultrasonically in acetone (15 min) prior to deposition.

In order to investigate the influence of processing conditions on the chemical characteristics of the coatings, several processing parameters were varied. Regarding the composition of the precursor solutions, parameters such as the relative and absolute precursor solute concentrations, the solution acidity (in terms of extra addition of nitric acid) and the type of precursor salt were investigated. Concerning the influence of apparatus-related deposition parameters on coating

properties, factors like the nozzle-to-substrate distance, the precursor liquid flow rate, the deposition temperature and the aforementioned nozzle geometry were studied.

The as-deposited ESD-coatings were subjected to rapid heat-treatments of 10–20 s in air at a temperature of 650 °C in an infrared furnace.[9] The as-deposited and heat-treated ESD-coatings were characterized using the following techniques:

1. Scanning electron microscopy (SEM): the surface morphology of the ESD-coatings was investigated using a JEOL 6310 SEM.
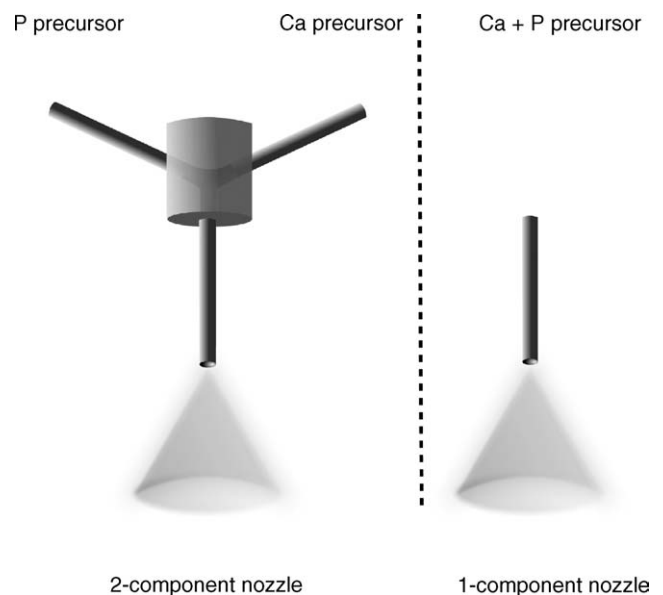2. Energy dispersive spectroscopy (EDS): the above described scanning electron microscope was equipped

Fig. 2. Conventional one-component and novel two-component spraying nozzle geometries.

with an energy-dispersive X-ray microanalyzer (Voyager). EDS was carried out at a magnification of 500× at an accelerating voltage of 10 kV in order to determine the elemental composition of the deposited coatings. Stoichiometric hydroxyapatite discs of known Ca/P ratio and of equal thickness to the coated Ti-substrates (1.5 mm) were used as a reference for the determination of Ca/P ratios of the deposited ESD-coatings.

3. X-ray diffraction (XRD): CaP coatings were subjected to X-ray diffraction analysis on a thin film Philips X-Ray Diffractometer using Cu Kα-radiation (PW 3710, 40 kV, 40 mA) in order to characterize the crystal structure of the deposited coatings. Coatings were analyzed by fixing the sample to a position of $2.5°$ and scanning the detector between $20° 2\theta$ and $50° 2\theta$ with a step-size of $0.02° 2\theta$, a scanning speed of $0.01° 2\theta/s$ and a sample time of 2 s/step.

4. Fourier-transform infrared spectrometry (FTIR): in order to characterize the molecular structure of the deposited coatings, infrared spectra of the films on the substrates were obtained from 4000 to 400 cm^{-1} by reflection Fourier-transform infrared spectrometry (Spectrum One, Perkin-Elmer), since infrared radiation cannot pass through the titanium substrate. The carbonate content of the deposited coatings was quantified according to a method as described by Featherstone[10], which uses infrared spectroscopy. Coatings were scraped off from the substrates and the resulting powder was used for quantification using a KBr method. This method allows carbonate estimation to better than ±10% in the range from 1 to 12 wt% carbonate.[10]

3. Results and discussion

3.1. Coating morphology of ESD-coating

In a previous study, it was shown that a wide range of CaP coating morphologies can be obtained.[11] As an example, Fig. 3 shows a scanning electron micrograph of a reticular
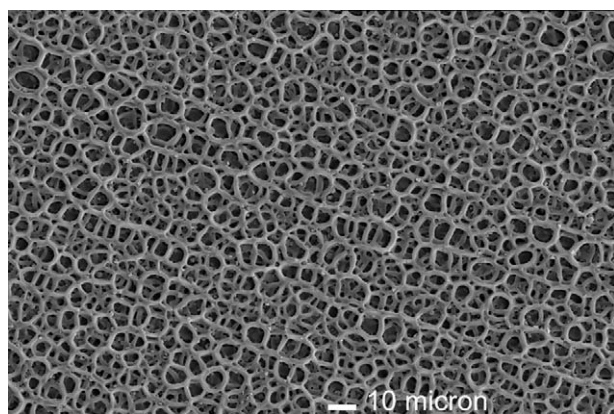

Fig. 3. SEM-micrograph of an ESD-deposited calcium phosphate coating, characterized by a porous surface morphology.

coating morphology characterized by an interconnected pore network.

3.2. Influence of the composition of precursor solutions on chemical properties

The results clearly showed that chemical properties of CaP coatings can be tailored by choosing the appropriate combination of deposition parameters. XRD and FTIR analyses revealed that various crystal phases and phase mixtures (metaphosphate, pyrophosphate, monetite, carbonate apatite (CO$_3$-Ap), carbonated hydroxyapatite (OH/CO$_3$-Ap), α/β-tricalcium phosphate (TCP), calcite, calcium oxide) were synthesized after heat-treatment.

The composition of the precursor solutions determined to a large extent the chemical properties of the deposited coatings. As an example of this influence, Fig. 4 shows the XRD-diffractograms (Fig. 4A) and corresponding FTIR-spectra (Fig. 4B) of coatings, deposited using various solution acidities (between 0 and 2.0 vol% of extra nitric acid). All as-deposited coatings were amorphous. After heat-treatment, various CaP crystal phases were obtained, depending on the acidity of the precursor solutions. Using the most acidic precursor solution (2% HNO$_3$), β-pyrophosphate was the main crystal phase (JCPDS File No. 9-346). However, diffraction peaks at $31.2°$ and $34.8° 2\theta$ were assigned to whitlockite corresponding to JCPDS File No. 13-404). Using less acidic precursor solutions (1% HNO$_3$), whitlockite was deposited with main reflections at $31.3°$ and $34.8° 2\theta$. A small peak at $31.8° 2\theta$ could be related to a minor contamination of apatitic nature. The XRD-pattern of the coating, deposited using a slightly acidic solution (0.1% HNO$_3$) corresponded to a poorly crystalline apatite phase. Without any addition of HNO$_3$, the crystal phase was also apatitic, but a shoulder at $37.5° 2\theta$ was assigned to calcium oxide as an impurity phase.

The FTIR-spectrum, corresponding to the most acidic deposition with 2% HNO$_3$, resembled the FTIR-spectrum of β-pyrophosphate, characterized by broad, feature-rich absorption bands between 900–1250 cm^{-1} (ν_3) and 450–650 cm^{-1} (ν_4). Small carbonate absorption peaks at 1482 and 1424 cm^{-1} were found in the IR-spectrum of coatings deposited with 1% of HNO$_3$. The ν_3 phosphate absorption band was less broad and feature-rich, and resembled the IR-spectrum of precipitated, Mg-containing whitlockite.[12] Using 0.1% of HNO$_3$, intense CO$_3$ absorption peaks at 878 (ν_2), 1415, 1453 and 1533 (ν_3) cm^{-1} indicated a considerable increase of carbonate incorporation. These ν_3 peaks indicated that carbonate anions were substituted for both phosphate (B-type) and hydroxyl groups (A-type) in a crystalline apatite lattice. The broad, featureless phosphate ν_3 band at 1050 cm^{-1} instead of a collection of sharply defined ν_3 absorptions was characteristic for poorly crystalline carbonate apatite. Absorption peaks at 960 (ν_1), 600 and 563 cm^{-1} (ν_4) were assigned to phosphate groups. Without any HNO$_3$, intense carbonate absorptions peaks at 874, 1414 and 1454 cm^{-1} corresponded to high carbonate content (B-type). Further,
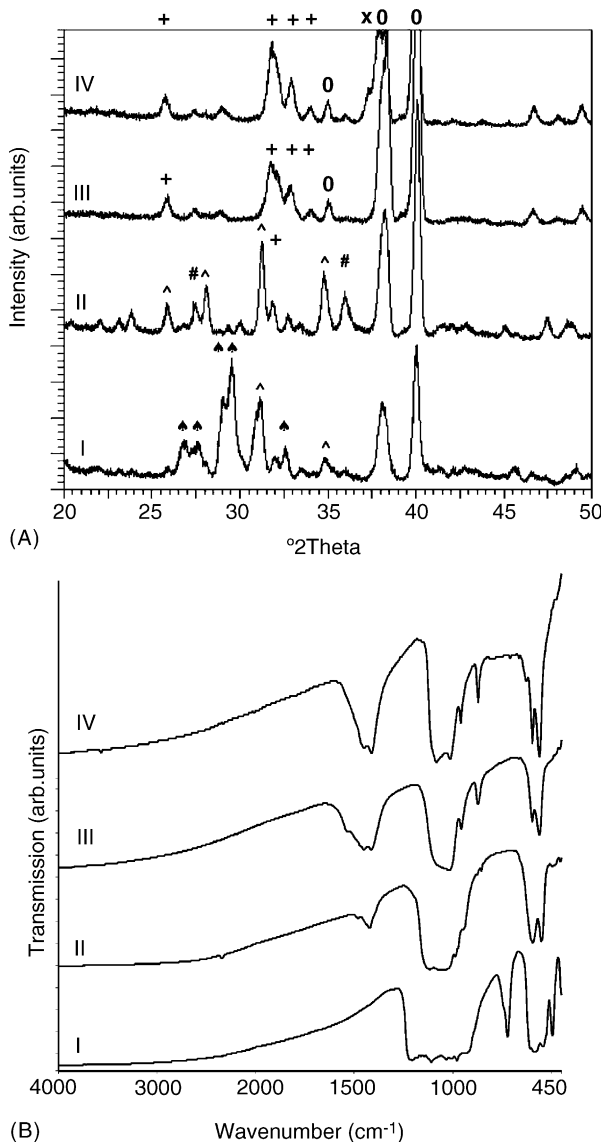
Fig. 4. (A): XRD-patterns of ESD-deposited calcium phosphate coatings, prepared using different acidities (in terms of HNO₃ addition) of the precursor solution. [I] 2 vol% of HNO₃ addition; [II] 1 vol% of HNO₃ addition; [III] 0.1 vol% of HNO₃ addition; and [IV] 0 vol% of HNO₃. (♠) β-pyrophosphate; (∧) whitlockite; (+) carbonate apatite; (#) rutile; (x) calcium oxide; (0) Ti. (B): FTIR-spectra (4000–400 cm⁻¹) of ESD-deposited calcium phosphate coatings, prepared using different acidities (in terms of HNO₃ addition) of the precursor solution. [I] 2.0 vol% of HNO₃ addition; [II] 1.0 vol% of HNO₃ addition; [III] 0.1 vol% of HNO₃ addition; and [IV] 0 vol% of HNO₃. Coatings were deposited using precursor solutions with a calcium nitrate concentration of 3.1 mM and a concentration of 1.9 mM phosphoric acid (Ca/P ratio 1.67), a liquid flow rate of 2.0 ml/h, a deposition temperature of 300 °C, a nozzle-to-substrate distance of 15 mm and a one-component nozzle geometry. All coatings were heat-treated at 650 °C.

small absorptions at 3570 and 630 cm⁻¹ were assigned to OH⁻ stretch and libration absorption modes. EDS revealed that Ca/P ratios of the deposited coatings were strongly dependent on the amount of HNO₃ added to the precursor solutions. Without any HNO₃, a very high Ca/P ratio of 3.4 was measured, whereas this value decreased to 1.1 for coat-

ings deposited using precursor solutions supplemented with 2.0 vol% of nitric acid.

The influence of other precursor solution parameters on chemical properties of ESD-derived CaP-coatings was described previously, to which the reader is referred for specific details.[13] On the basis of these results, however, a chemical mechanism of coating formation was proposed. Briefly, the deposition of the various crystal phases was suggested to be the result of the following acid–base reaction between basic CO_3^{2-} groups (originating from solvent decomposition reactions) and acidic HPO_4^{2-} groups from an intermediate monetite ($CaHPO_4$) phase of the CaP precipitate:

$$2HPO_4^{2-} + CO_3^{2-} \rightarrow 2PO_4^{3-} + CO_2 + H_2O$$
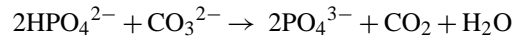
Evidence for the relevance of this intermediate monetite phase was three-fold. First of all, it was observed by means of precipitation experiments that the monetite phase was formed upon precipitation of calcium and phosphate precursor solutes in the organic solvent butyl carbitol (at various absolute and/or relative concentrations).[13] This observation was confirmed by the fact that the interior of all spraying nozzles was covered with a thin layer of monetite after several tenths of hours of operation, as characterized by means of FTIR (Fig. 5). The FTIR-spectrum of the precipitate from the interior of the nozzle was identical to the IR-spectrum of pure monetite.[12] Thirdly, monetite coatings were deposited using highly concentrated – and consequently rapidly precipitating – precursor solutions.[13] Moreover, from literature, it is known that monetite reacts in hot carbonate solutions yielding an apatite phase, often with simultaneous formation of calcite.[14]

It was concluded that carbonate ions play an essential role in controlling the chemical properties of the deposited ESD-coatings. The amount of carbonate incorporation (ranging from 0 to 15 wt% as quantified by means of an infrared method[10]) determined the crystal and molecular structure of the deposited coatings. At low concentrations, carbonate acts as a base that eliminates protons from acidic, hydrogenated phosphate groups. With increasing carbonate content, carbonate is incorporated into apatitic calcium phosphate
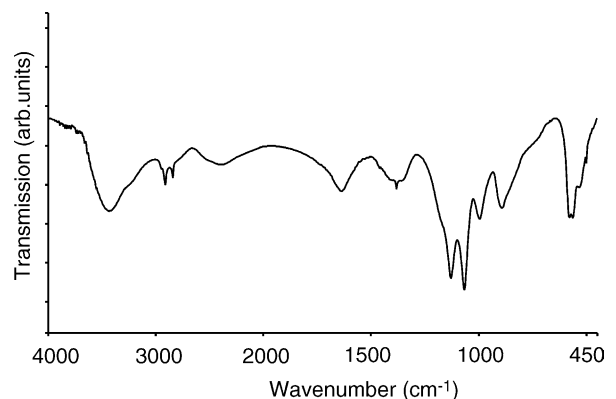

Fig. 5. FTIR-spectrum of precipitate obtained from the interior of a two-component spraying nozzle after several tenths of hours of operation.

phases. At a higher carbonate wt% (typically more than 10 wt% CO_3), an extra calcite phase is formed as a result of a reaction between excessive Ca^{2+} cations and $CO_3{}^{2-}$ anions.

3.3. Influence of apparatus-related deposition parameters

The chemical properties of ESD-coatings appeared to be dependent also on apparatus-related parameters. As an example of this influence, Fig. 6 shows the FTIR-spectra of as-deposited coatings, synthesized at different deposition temperatures. The minimum deposition temperature for the formation of CaP coatings by means of ESD was 300 °C; at lower temperatures, it was impossible to obtain solid, ceramic coatings. Thus, it was concluded that formation of CaP coatings was not just the result of solvent evaporation, since the boiling point of the solvent butyl carbitol ($C_8H_{18}O_3$) of 231 °C was significantly lower than 300 °C. This indicated that a chemical reaction was needed for coating formation. Remnants of the organic solvent were still present at 300 °C, as indicated by several absorption peaks,[15] such as intense CH stretch absorptions (between 2850 and 2940 cm^{-1}), a CH bending band at 1460 cm^{-1}, a symmetric CH bending band of the CH_3 group at 1376 cm^{-1}, and a CH_2 rocking absorption at 722 cm^{-1}. Moreover, an absorption peak at 1713 cm^{-1} was assigned to C=O. At a deposition temperature of 350 °C, the organic remnants and C=O groups were absent and two broad ν_3 carbonate absorptions were observed at 1487 and 1425 cm^{-1}. Also, a small ν_2 carbonate peak at 870 cm^{-1} was found. These vibrations correspond to carbonate groups engaged in an amorphous CaP environment.[16]
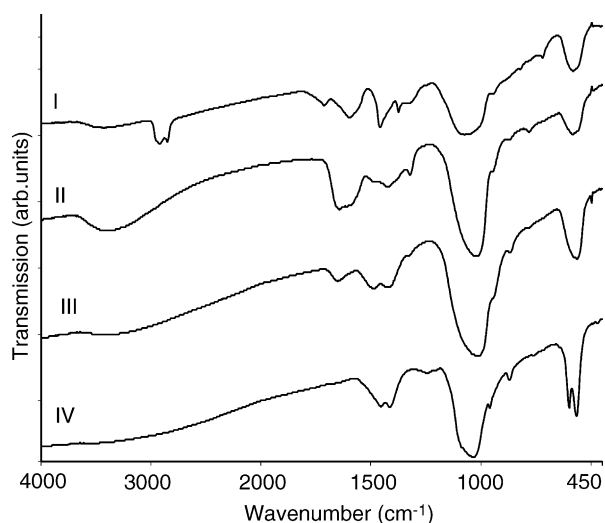

Fig. 6. FTIR-spectrum (4000–400 cm^{-1}) of ESD-deposited calcium phosphate coatings, prepared at different deposition temperatures. [I] 300 °C; [II] 350 °C; [III] 450 °C; and [IV] 600 °C. Coatings were deposited using a two-component nozzle geometry with separate inlets for the calcium precursor solution (calcium nitrate at a concentration of 5.0 mM in butyl carbitol) and the phosphate precursor solution (phosphoric acid at a concentration of 3.6 mM in butyl carbitol) (Ca/P ratio 1.4), a liquid flow rate of 1.0 ml/h and a nozzle-to-substrate distance of 20 mm. All coatings were as-deposited.

Moreover, absorption peaks at 782, 1323 and 1646 cm^{-1} corresponded to the presence of hydrated calcium oxalate.[17] At a deposition temperature of 450 °C, the oxalate absorption peaks were hardly visible anymore. On the contrary, the carbonate bands at 1488, 1425 and 870 cm^{-1} were still present. It was concluded that carbonate ions were formed via intermediate oxalate groups as the result of thermal decomposition of the organic solvent butyl carbitol. From literature, it is known that oxalate decomposes to carbonate around 425 °C according to the following reaction[18]:

$$C_2O_4{}^{2-} \rightarrow CO_3{}^{2-} + CO$$
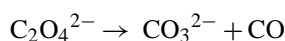
Phosphate absorptions between 1250–900 cm^{-1} (ν_3) and 650–500 cm^{-1} (ν_4) remained broad and unsplit up to deposition temperatures of 550 °C, but at 600 °C, these two absorption bands split up into sharper bands at 1087, 1032 (ν_3), 962 (ν_1), 602 and 567 cm^{-1} (ν_4). Furthermore, sharp carbonate bands (ν_3) at 1455 and 1416 cm^{-1} revealed that carbonate was mainly substituting for phosphate anions (B-type substitutions) in a crystalline CaP environment. By means of XRD analysis, the crystalline apatitic structure of these coatings was confirmed, since main reflection lines were located at 25.8°, 31.9° and 32.9° 2θ, which correspond to (0 0 2), (2 1 1) and (3 0 0) reflections of the apatite structure.[12] This indicated that the as-deposited coatings remained amorphous up to deposition temperatures of 600 °C, which was the minimum temperature for crystallization of these B-type carbonate apatite coatings. Generally, all coatings transformed into crystalline carbonate apatite (CA) after additional heat-treatment at 650 °C, irrespective of their initial deposition temperature, indicating that the deposition temperature did not influence the final chemical structure of the heat-treated coatings.

Regarding the influence of the nozzle-to-substrate distance, it was concluded that the carbonate concentration of the deposited CaP coatings decreased with increasing nozzle-to-substrate distance (data not shown). As a result, various phases and phase mixtures of carbonate apatite and/or tricalcium phosphate were deposited. However, no solid physical explanation was found yet for this relationship between nozzle-to-substrate distance and the amount of carbonate incorporation.

Regarding the influence of the liquid flow rate on the chemical structure of deposited coatings, relevant FTIR-spectra of heat-treated coatings are shown in Fig. 7A. At a flow rate of 1.0 ml/h, a small ν_2 absorption at 879 cm^{-1} and three ν_3 absorptions at 1414, 1456 and 1546 cm^{-1} were assigned to carbonate ions substituting for hydroxyl (A-type) and phosphate groups (B-type). Phosphate peaks were located at 1055 (ν_3), 961 (ν_1), 600 and 567 cm^{-1} (ν_4). At a lower flow rate of 0.5 ml/h, carbonate peaks were considerably more intense. Only B-type substitutions were left (peaks at 1456 and 1416 cm^{-1})—absorption peaks corresponding to A-type substitutions were not detected. At 0.5 ml/h, phosphate absorptions were more sharpened as compared to the
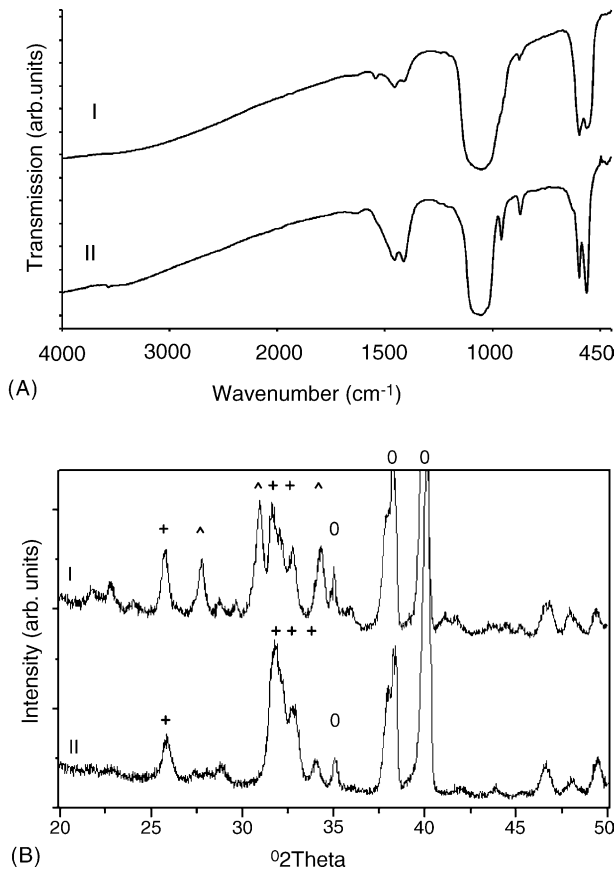
Fig. 7. (A): FTIR-spectra (4000–400 cm^{-1}) of ESD-deposited calcium phosphate coatings, prepared at different liquid flow rates. [I] 1.0 ml/h and [II] 0.5 ml/h. (B): XRD-patterns of ESD-deposited calcium phosphate coatings, prepared at different liquid flow rates. [I] 1.0 ml/h and [II] 0.5 ml/h. Coatings were deposited using a two-component nozzle geometry with separate inlets for the calcium precursor solution (calcium nitrate at a concentration of 5.0 mM in butyl carbitol) and the phosphate precursor solution (phosphoric acid at a concentration of 3.6 mM in butyl carbitol) (Ca/P ratio 1.4), a deposition temperature of 340 °C, and a nozzle-to-substrate distance of 20 mm. All coatings were heat-treated at 650 °C. (∧) β-TCP; (+) carbonate apatite; (0) Ti; (#) rutile.

higher flow rate of 1.0 ml/h. Quantification of carbonate concentrations was performed using precursor solutions with Ca/P ratios varying between 1.7 and 1.9. Using a high flow rate of 1.0 ml/h, CO_3 concentrations were measured between 5 and 9 wt%, whereas considerably higher values between 13 and 15 wt% were quantified using a lower flow rate of 0.5 ml/h. In these cases, minor IR-absorption peaks of a secondary calcite phase were observed at 713 cm^{-1}.

XRD revealed that a phase mixture was deposited consisting of CA and a considerable amount of β-TCP using a flow rate of 1.0 ml/h, whereas phase pure CA without any trace of β-TCP was deposited at a flow rate of 0.5 ml/h (Fig. 7B). It was suggested that the observed chemical differences were caused by different precursor mixing times for both flow rates. In order to study the mixing behavior of the precursor solutions, experiments were carried out in which the pH of stirred and unstirred precursor solution mixtures was

monitored during mixing. Generally, a pronounced and time-dependent pH-drop of several pH-values was observed for both stirred and unstirred precursor solution mixtures within the first few minutes of mixing (data not shown). In other words, the H$^+$ concentration increased upon mixing due to dissociation of protons from acid phosphate groups, such as H_3PO_4 and $H_2PO_4^-$. Consequently, the total negative charge of dissolved phosphate anions gradually increased upon mixing of both precursor solutions as a result of a time-dependent shift of the phosphate equilibrium towards the basic direction:

$$H_3PO_4 \rightarrow PO_4^{3-} + 3H^+$$

Due to the time-dependent equilibrium position of this reaction, the average negative charge of the phosphate ions in the spraying cone was expected to be smaller using a high flow rate with a short mixing time as compared to a low flow rate with a long mixing time.

The importance of precursor mixing times for the chemical characteristics of ESD-coatings was further confirmed by the observation that carbonate concentrations were considerably larger for one-component nozzle geometries with long mixing times of more than 45 min, as compared to the two-component nozzle geometry with a reduced mixing time of ±60 s (Fig. 8). Again, this difference could be explained by the aforementioned, time-dependent pH-drop upon mixing of the precursor components.

In order to give an overview of the influence of deposition parameters on ESD-coating chemistry, the effects of several parameters on the chemical characteristics of deposited coatings are summarized in Table 1.
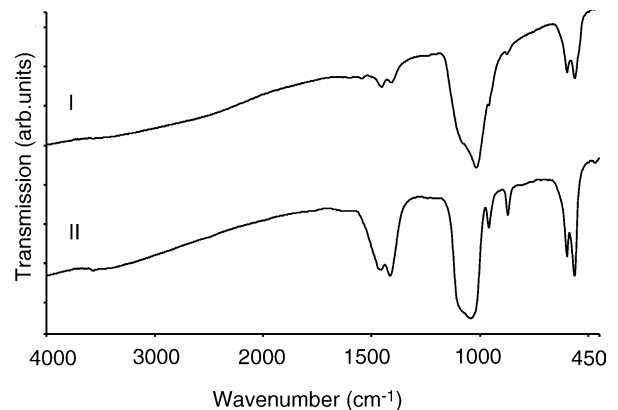

Fig. 8. FTIR-spectra (4000–400 cm^{-1}) of ESD-deposited calcium phosphate coatings, prepared using different nozzle geometries. [I] Two-component nozzle geometry and [II] one-component nozzle geometry. Coatings were deposited using a calcium precurcor solution of 5.0 mM calcium nitrate in butyl carbitol and a phosphate precursor solutions of 3.6 mM phosphoric acid in butyl carbitol (Ca/P ratio 1.4). Both precursor solutions were either premixed (one-component nozzle) or inserted separately (two-component nozzle). The deposition temperature was 340 °C, the flow rate was either 1.0 ml/h (two-component nozzle) or 2.0 ml/h (one-component nozzle) and the nozzle-to-substrate distance was 20 mm. All coatings were heat-treated at 650 °C.

Table 1
Qualitative effects of several deposition parameters on crystal structure, carbonate content and Ca/P ratio of ESD-deposited coatings (after heat-treatment)

Deposition parameter		Crystal phase	Carbonate content	Ca/P ratio of coating
Precursor solution acidity	0 vol% HNO_3	Carbonate apatite (+traces of CaO)	High	3.3–3.4
	0.1 vol% HNO_3	Carbonate apatite	Intermediate	2.0–2.1
	1.0 vol% HNO_3	Whitlockite (+ traces of carbonate apatite)	Low/absent	1.3–1.4
	0 vol% HNO_3	β-Pyrophosphate	Absent	1.0–1.1
Deposition temperature	300 °C	Carbonate apatite	Intermediate	1.9–2.0
	350 °C	Carbonate apatite	Intermediate	1.9–2.0
	450 °C	Carbonate apatite	Intermediate	1.9–2.0
	600 °C	Carbonate apatite	Intermediate	2.0–2.1
Nozzle-to-substrate distance	5 mm	Carbonate apatite	High	2.2–2.3
	10 mm	Carbonate apatite (+ traces of β-TCP)	Low	1.7–1.8
	40 mm	β-TCP/carbonate apatite	Low/absent	1.6–1.7
Liquid flow rate	0.5 ml/h	Carbonate apatite	High	2.0–2.1
	1.0 ml/h	β-TCP/carbonate apatite	Low	1.7–1.8
Nozzle geometry	One-component	Carbonate apatite	High	2.1–2.2
	Two-component	Carbonate apatite (+ traces of β-TCP)	Low	1.8–1.9

4. Conclusion

On the basis of the results, we conclude that the ESD technique is very appropriate to deposit calcium phosphate coatings with a large variety of chemical properties onto biomedical substrate materials. The chemical properties of the coatings were determined by both physical, apparatus-related factors and chemical, solution-related parameters. In general, it was concluded that ESD is especially suitable in research focused on the fundamental relationship between CaP coating characteristics and biological coating performance due to the versatility of the technique regarding deposition of coatings with tailored chemical properties.

Acknowledgement

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