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Calcium phosphate coatings prepared by aerosol-gel

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Abstract

The aerosol-gel process has been assayed for the deposition of calcium phosphate (CaP) coatings. The deposition conditions have been preliminarily studied in order to obtain polycrystalline hydroxyapatite (HAP) coatings. The evolution of composition, structure and morphology was monitored by FTIR, XRD and SEM techniques as a function of the sintering temperature. HAP coatings deposited on TiAlV substrates were further characterized by Auger and indentation techniques in order to measure their quantitative composition and adhesive strength, respectively. The results corroborate the high quality of aerosol-gel derived HAP coatings.
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1. Introduction

The quest for new generation implants able to promote osseointegration and having longer lifetimes has attracted much interest in the study of hydroxyapatite [HAP, $Ca_{10}(PO_4)_6(OH)_2$]. The bioactive properties of this mineral have shown to provide a faster fixation of the implants.[1] Sol-gel HAP has already been processed in the form of films (deposited via dip[2–4] or spin-coating[5]) as well as in the form of powders.[6] A general view of the processes that lead to the formation of phosphate sols is presented by Livage et al.[7] and a formal polymerization route has been presented by Brendel et al.[2]

The objective of this work is to prepare adherent HAP films by the aerosol-gel process from the previously excluded triethyl-phosphate (TEP) precursors. The main reason for this exclusion is the low rate of hydrolysis of this precursor, induced by the weakly positive partial charge of the phosphate.[7] The aerosol-gel process has been recently used to deposit biocompatible titania coatings and optical grade films for antireflective applications.[8,9] The method introduces some extra advantages over dip and spin coating making the process compatible with in-line technologies. Regarding the process itself, the main advantage is that in the aerosol-gel route deposition and evaporation steps do not overlap (this enhances greatly coating homogeneity and reproducibility). In addition, it lends itself to the deposition on large and three-dimensional substrates, which is essential for the processing of elements of complex design such as hip-joint prostheses.

2. Experimental procedure

Thin films were deposited from calcium nitrate [$Ca(NO_3)_2.4H_2O$] and triethylphosphate [TEP, $(C_2H_5)_3PO_4$] diluted in ethanol. The precursors were diluted separately and heated for 24 h at 60 °C after mixing. Solutions with a Ca concentration of 0.625 mol/l and P concentrations of 0.375, 0.78 and 1.25 mol/l (Ca/P mr: 1.67, 0.8 and 0.5) were compatible with ultrasonic nebulization. (100) silicon wafers and TiAlV plates were used as substrates.

After production of a steady state aerosol, the microdroplets were conducted into the deposition chamber by an air flux. After 3 min, homogeneous liquid films were obtained and then stabilized at 500 °C for 5 min. This

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treatment was performed before the formation of a xerogel film. Deposition/stabilization treatment cycles were repeated ten times in order to obtain films of 5 μm thickness. The coatings were finally sintered in air for 15 min at 500, 800 and 1000 °C. The coatings are labeled as in the following example: CP-167-800 refers to a coating from a solution with Ca/P = 1.67 and sintered at 800 °C.

The characterization of the coatings has been carried out by using FTIR (Bio-Rad FTS165 spectrometer, 4 cm^{-1} resolution), XRD (θ/2θ Siemens CuK_α, 6 s integration, 0.04° step) and SEM (Phillips XL30 15 kV). Auger spectra were obtained after 5 min Ar^+ bombardment in a JEOL system (JAMP-10S, e^- probe diameter 0.1 mm, 5 KeV) on HAP coated TiAlV plates and on a HAP standard (Strem chemicals).

The adherence of these coatings was tested by an indentation method.[10] In porous materials failure takes place by the propagation of complex fractures. We monitored the load and displacement of the probe to provide a reliable detection of the failure point. Indentations were performed with a Shimadzu DUH-200 dynamic ultra microhardness tester (0.02 mN load and 0.005 μm depth resolutions) applying 20 loading–unloading tests (30 mN maximal load, 0.3 mN/s). The failure load (L_f) and failure depth (d_f) were found to be the most relevant parameters to determine the adhesive strength from the estimation of the area of contact.[11]

3. Results

In order to determine the conditions that lead to HAP, an extensive characterization of the coatings issued from different Ca/P mr solutions and sintering temperatures was performed. The best results in terms of HAP formation were obtained for precursors with a Ca/P mr of 0.8. The description of the results will be thus focussed in the description of these films.

Characteristic FTIR HAP absorption bands[12] were observed in all CP-80-T coatings (Fig. 1). Structural hydroxyl groups generate bands at 3570, 630 and a shoulder at 335 cm^{-1}. Bands located in the range 1030–1090 cm^{-1} and at 960, 605, 570 and 470 cm^{-1} are coincident with phosphate group absorption. CaO bands at 940 and 720 cm^{-1} and carbonate compounds at 1455, 1420 and 875 cm^{-1} were also identified. Carbonate bands observed in CP-80–500 coatings present moderate intensities (875 cm^{-1}, Fig. 1a). Coatings sintered at 800 °C evidence an important exchange in relative absorbance between the carbonate bands at 1455 and 1420 cm^{-1} (Fig. 1b). In addition, the hydroxyl bands suffer a slight increase.

The CP-167-T coatings were discarded as HAP coatings since the spectra (Fig. 1c) revealed increased absorption of the carbonate and CaO bands in comparison with CP-80-T coatings. Lowering the solution Ca/P mr down to 0.5 (CP-50-800, Fig. 1d) lead also to undesirable changes in the films such as a lower hydroxylation degree and partial shifts of the most important HAP bands (from 1030 to 1025 cm^{-1}). However, the carbonate content decreased with respect to CP-80-800.

The analysis by XRD evidences the presence of polycrystalline phases. The CP-80-500 coating is composed of HAP and $CaCO_3$ (CaCb) as a minor component (Fig. 2a). Sintering at 800 °C produces reflections due to CaO [(200) peak, 37.3°] replacing the CaCb peaks (Fig. 2b). In the CP-80–1000 coating pattern, CaO peaks are still present indicating the stability of this compound (Fig. 2c). It is worth mentioning that even at this temperature there is no segregation of the HAP phase, which further proves the high quality of the coating. Another remarkable feature is that the crystallite size in the HAP coating has notably increased at this temperature (lower FWHM). Concerning the samples

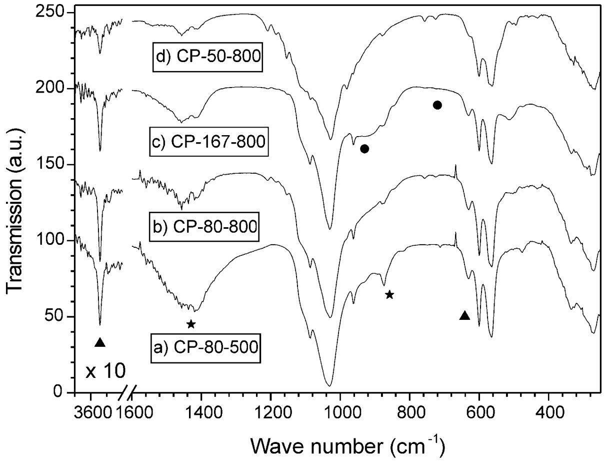

Fig. 1. FTIR spectra of coatings: (a) CP-80-500, (b) CP-80-800, (c) CP-167-800 and (d) CP-167-800. ▲: OH, ⋆: CO_3, •: CaO.

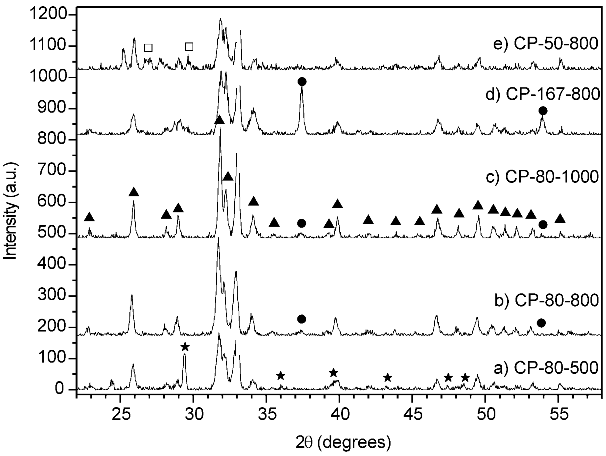

Fig. 2. XRD patterns of coatings: (a) CP-80-500, (b) CP-80-800, (c) CP-80-1000, (d) CP-167-800 and (d) CP-50-800. ▲: HAP, ⋆: CaCb, •: CaO, □: βTCP.

prepared with other stoichiometries, the peaks in the CP-167-800 patterns (Fig. 2d) evidenced a much higher CaO contribution. For CP-50-800 coatings (Fig. 2e), new CaP compounds have been evidenced (βTCP).

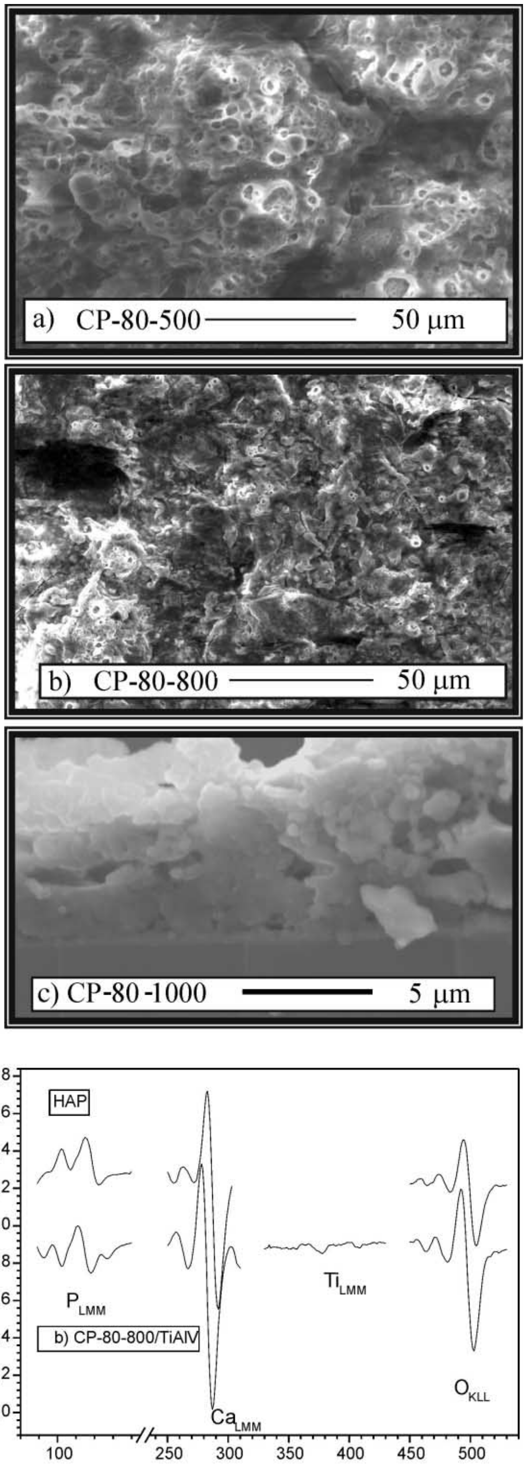

Fig. 3. (a–c) SEM micrographs of the CP-80-T coatings; (b) Auger spectra of an HAP standard and a CP-80-800/TiAlV coatings in the spectral region corresponding to P_{LMM}, Ca_{LMM}, Ti_{LMM} and O_{KLL} transitions.

The SEM images presented in Fig. 3 show the high porosity of the CaP coatings. For increasing temperatures (i.e. from 500 to 800 °C), a granule coalescence process drastically reduced the surface roughness (Fig. 3a and b) although the root mean square roughness values remained always higher than 0.4 μm when scanning over areas of 10×10 μm^2. Additionally, a large pore size distribution (1–10 μm) can be observed in the cross section image of CP-80-1000 coatings (Fig. 3c). The coating is formed of granules leaving internal voids that produce the highly porous structure.

The Auger spectrum of the CP-80-800/TiAlV coating presents slightly higher peak to peak intensities at the Ca_{LMM} transition than the HAP standard (Fig. 3b). The coating contains a Ca concentration 11% higher than the one corresponding to the HAP standard. The O_{KLL} transition presents also a higher intensity in the CP-80-800/TiAlV sample. A chemical shift, specially accused in the Ca transition, can be assigned to a preferential charging process in the HAP standard.

Fig. 4 presents the typical loading curve obtained in the adhesive strength tests. In the first indentation steps, small instabilities are observed due to friction phenomena. The load follows then a semi-hyperbolic dependence until depths of approximately 1 μm are reached. From there on, a point of inflexion appears, the slope diminishes and a drastic jump related to the catastrophic failure of the coating is observed. The loading process continues then until the maximal load is reached. Finally, the probe recovers freely as denoted by the almost vertical unloading process. Special attention was paid to avoid the probe to approximate the TiAlV substrate. The data obtained from twenty indentations show that the mean L_f is 11.0 mN (minimal L_f 5.60 mN) and the mean d_f is 1.15 μm (minimal d_f 0.75 μm). These

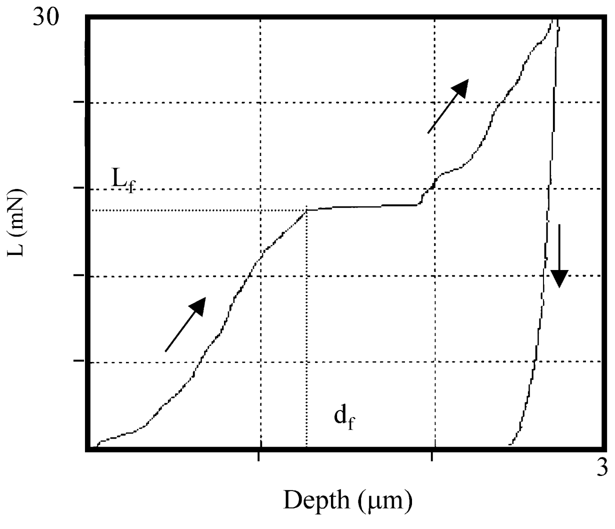

Fig. 4. Adhesive strength tests performed by indentation on the CP-80-800/TiAlV coating (30 mN maximal load).

values suggest, via calculus of the area of contact, that the coating adhesive strength is in the order of 100 MPa.

4. Summary and conclusions

Calcium phosphate coatings can be formed by the aerosol-gel process from $Ca(NO_3)_2$ and TEP precursors. It is possible to overcome the low sol-gel reactivity of the TEP precursor by applying a stabilization heat treatment at 500 °C. For the preparation of porous polycrystalline HAP films, the Ca/P mr of the solution can be optimized around 0.8. The presence of satellite phases is influenced by the Ca/P mr of the solution and by the sintering temperature. The behavior of IR bands assigned to carbonate groups indicate the presence of two carbonated phases. On one side, the inclusion of carbonate groups in the apatite structure and on the other, the presence of a CaCb phase. However we have shown that this latter fase can be minimized. In fact, the lower the Ca/P mr of the precursor solution, the less important is the formation of CaCb and the lower is the CaO content after calcination at 800 °C. This suggests that the amount of phosphate in the sol determines the quantity of CaCb formed during stabilization at 500 °C (since Ca concentration remains constant). Moreover, it implies that the TEP precursor is enough reactive so as to be more avid for Ca atoms than the carbonate groups formed during stabilisation. Concerning the carbonate integrated in HAP structure, the slight rehydroxylation of the CP-80-T structures after sintering from 500 to 800 °C is undoubtedly due to the OH substitution of carbonate groups stabilized in the natural hydroxyl site. Auger spectra measured for such CaP coatings deposited on TiAlV alloys confirm a good agreement with the composition of the HAP standard. Slight deviations imply a weak Ca overstoichiometry, which is compatible with the presence of a CaO phase (XRD) and also with a partial substitution of carbonate in the HAP phosphate site.

The adhesive strength, measured by means of indentation techniques, was found to be in the order of 100 MPa, which is significantly higher than the value obtained for equivalent HAP coatings.[3,4] This difference can be partially influenced by local effects in the indentation measurement method. It is worth mentioning that no drastic structural or compositional differences were found between our coatings and those appearing in the previously mentioned works. This similarity becomes evident when comparing the XRD diagrams of the HAP coatings, which present a clear CaO contribution (although not mentioned or erroneously ascribed to the TiAlV substrate). However, relevant morphological differences were evidenced at the surface[4] and interface[3] respectively.

These results are considered of primary interest since aerosol-gel processing allows the deposition on complex substrates, which are constantly required in prosthetic applications.

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