

Fluorapatite coatings by metal organic chemical vapor deposition

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The metal organic chemical vapor deposition technique is used for the production of fluorapatite coatings using titanium as substrate and yttrium oxide as a passive diffusion barrier.

There has currently been tremendous interest in designing new materials to be used in repairing and reconstructing diseased or damaged parts of the human body. In this context great interest has been devoted to the study of some calcium phosphate-based materials, initially chosen for their chemical similarity to the main bone-constituting inorganic compounds,¹ whose *in vivo* behavior has been defined as bioactive.² Hydroxyapatite [HAP, $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$] and fluorapatite [FAP, $\text{Ca}_5(\text{PO}_4)_3\text{F}$] are two of the more commonly used ceramics for clinical applications. They show typical bioactive behavior *in vivo* generating direct contact between the bone and the ceramic surface with no fibrous tissue layer intervention.³ Unfortunately though, poor mechanical properties prevent their use as load-bearing implants and considerable research has thus been directed towards the development of calcium phosphate-based coatings on high strength substrates for prosthetic applications involving complex loading arrangements.⁴ In the last few years equal efforts have been made in the study and optimisation of HAP-based coatings and, more recently, FAP coatings have been produced. FAP is more stable than HAP at high temperatures⁵ and has been seen to have favorable biological characteristics.^{6,7}

The plasma spraying technique (PLS), first introduced by De Groot *et al.*,⁸ is the most thoroughly investigated method for the production of calcium phosphate-based coatings. However, the high temperature (in the region of 10 000 K) at which the ceramic powder is maintained during the process, generates the partial decomposition of the precursor compounds. This is not easily controlled and amorphous phases are formed.^{9,10} The above limitations have led to the development of new synthetic routes with the aim of increasing control of the different chemical and physical characteristics of the coatings such as stoichiometry, crystallinity, thickness and surface composition.

We report the use of metal organic chemical vapor deposition (MOCVD) as a new technique for the production of FAP coatings and as an alternative to PLS. The MOCVD technique is a widely used technique in both applicative and research fields, being based on the production of solid coatings from the chemical reactions of gaseous or vaporized metal-organic compounds.¹¹ Various features make this useful for the production of thick coatings on complex shaped objects. The possibility of 'chemically' and kinetically controlling the deposition process throughout its course and the scope for large-scale production^{11,12} are also important aspects which make this technique extremely promising for bioceramic coating production. When compared to PLS, MOCVD allows improved control of coating characteristics as the type of nucleation and growth, the deposition rate and the final stoichiometry of the coating can be modulated.¹¹

The experiments were carried out with a horizontal hot-wall reactor[†] using $\text{Ca}(\text{hfa})_2$ -tetraglyme (Hhfa = 1,1,1,5,5,5-hexafluoropentane-2,4-dione, tetraglyme = 2,5,8,11,14-pentaoxapentadecane) and diphenylphosphinic acid (dppa) (Aldrich) as volatile precursors. Titanium was used as the substrate

(Goodfellow). To prevent deleterious effects due to the formation of an interfacial layer made up of titanium oxide, the exposed surface was modified by the application of an MOCVD-deposited diffusion barrier constituted of yttrium oxide (Y_2O_3).[‡] For all the samples, coatings of FAP were obtained, following a double-step deposition process. The coatings made up of calcium fluoride (CaF_2),[§] obtained after the first step, were transformed into FAP after treatment with dppa vapor. During the latter step the highest substrate temperature throughout the process was reached (550 °C). This double step made a modulation of the FAP/ CaF_2 ratio possible by controlling the time of exposure to dppa vapor.

For all the samples X-ray diffraction (XRD)[¶] patterns clearly showed the presence of polycrystalline FAP (Fig. 1) whose average crystallite size was estimated using the Scherrer formula: $t = 0.9\lambda/(B\cos\theta)$ where t is the crystallite size, λ is the X-ray wavelength, B is the full width at half maximum (FWHM) and θ is the X-ray angle of incidence at the Bragg condition angle for the selected peak. This formula roughly evaluates the size of the coherent crystallite domains by considering how the decrease in size of the crystallite causes an extension of the diffracted line beyond instrumental broadening. When considering the (002) reflection an average crystallite size of ca. 400 Å was estimated for the coatings deposited in the reported conditions.[†] Surface morphology was probed by atomic force microscopy (AFM).^{||} The investigation showed the presence of round particles with a diameter in the range of a few hundred nanometers. Distortion effects, induced by the tip geometry and by tip-sample interactions, that could partially alter the real particle diameters, have not been considered.¹³

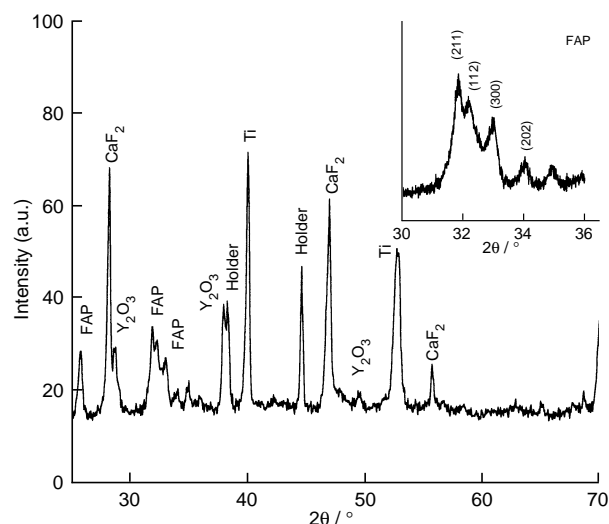


Fig. 1 X-Ray diffraction pattern obtained from Y_2O_3 -coated titanium after fluorapatite deposition. The spectrum obtained using $\text{Cu-K}\alpha$ radiation clearly shows the presence of titanium and Y_2O_3 together with CaF_2 and FAP. Two peaks attributed to the aluminium holder are also shown. The transformation of CaF_2 to the crystalline FAP is a consequence of exposure to diphenylphosphinic acid vapor at 550 °C. The characteristic features of the FAP reflections included in the range $2\theta = 30\text{--}36^\circ$ are highlighted.

This evidence, together with the XRD results, suggests that crystallites bind to form these particles.

Deposition rate, evaluated in the range of $0.5\text{--}1\ \mu\text{m h}^{-1}$, was estimated by examining X-ray photoelectron spectroscopy (XPS) depth profiles** after calibrating the sputter rate for the coatings using the Rutherford backscattering spectroscopy.††

The study of substrate/coating interfaces is of great relevance for problems concerning adhesion to the substrate. X-Ray photoelectron spectroscopy depth profiles were used to investigate the FAP/substrate interface when titanium was the substrate and Y_2O_3 was the diffusion barrier. The analyses (Fig. 2) showed the presence of an yttrium-containing layer which slowed titanium diffusion. This was a consequence of the thermodynamic stability of Y_2O_3 which is more stable than titanium and therefore allows a passive diffusion barrier to form for the titanium itself.¹⁴ The relatively broad distribution of the yttrium layer and the presence of calcium, oxygen and phosphorus with only a slight decrease in concentration with depth (sputtering time) may indicate a partial substitution of the yttrium in the FAP structure. Unfortunately, no evidence for this substitution was observed in the XRD pattern.

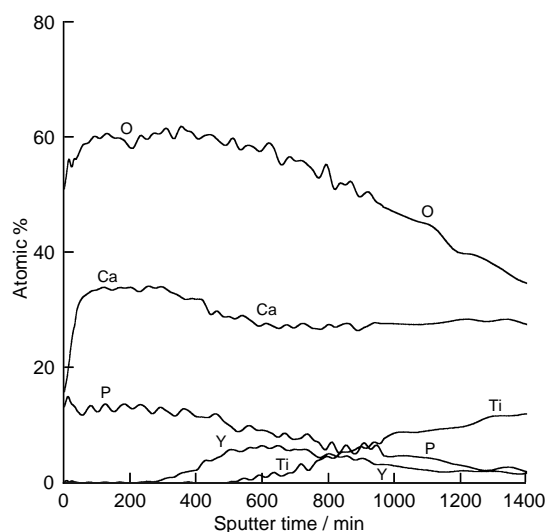


Fig. 2 X-Ray photoelectron spectroscopy depth profile of a Y_2O_3 -coated titanium substrate after fluorapatite deposition. Signals due to the yttrium layer appear after 200 min of Ar^+ sputtering, increasing in intensity up to 600 min of sputtering. Titanium diffusion towards the surface is stopped according to maximum yttrium concentration.

MOCVD is thus proposed as a new technique for the production of FAP coatings. This technique makes it possible to produce FAP coatings whose properties fit relevant properties for biomaterial coatings. In fact, the coatings are crystalline with a particle diameter in the same range as that of suitable biomaterials.¹⁵ The use of proper diffusion barriers also reduces unwanted effects due to the formation of a brittle interface between the substrate and the coating. A positive point to be underlined is the lower temperature maintained during deposition in comparison with the temperature reached with the PLS technique.

We are now further optimizing the deposition parameters with the aim to increase the deposition rate. We are also testing various diffusion barriers in an attempt to produce coatings with increased performances.

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Footnotes and References

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† The reactor chamber was constituted by a quartz tube. During the depositions a total pressure of 10 Torr was maintained in the chamber while

a continuous flux of Ar ($50\ \text{ml min}^{-1}$) was used as carrier for the sublimed precursors. A temperature of $85\ ^\circ\text{C}$ was maintained in the sublimation region of the reactor for the $\text{Ca}(\text{hfa})_2$ -tetraglyme adduct and dpaa was sublimed at a temperature of $185\ ^\circ\text{C}$. The highest temperature reached during the experiments in the deposition region in which the substrate to be coated was placed was $550\ ^\circ\text{C}$. For a detailed description of the synthetic procedure used for $\text{Ca}(\text{hfa})_2$ -tetraglyme adduct see: G. Malandrino, F. Castelli and I. L. Fragalà, *Inorg. Chim. Acta*, 1994, **224**, 203.

‡ Yttrium oxide was deposited using $[\text{Y}(\text{dpm})_3]$ (Aldrich) as the volatile precursor maintaining the substrate to be coated at $300\ ^\circ\text{C}$ with Ar flux ($50\ \text{ml min}^{-1}$) used as carrier. The total pressure in the reactor during deposition was 10 Torr. A temperature of $165\ ^\circ\text{C}$ was maintained in the sublimation region of the reactor during deposition.

§ The CaF_2 coatings were characterized by XRD and XPS; XRD spectra showed their highly crystalline nature with no preferred orientation structure. XPS confirmed the presence of Ca and F on the surface of the coatings with carbon, oxygen and silicon impurities. The atomic ratio Ca/F was ca. 0.5.

¶ X-Ray diffraction measurements (Ni-filtered $\text{Cu-K}\alpha$ radiation) were made for the coated samples placed in aluminium sample holders, and scanned with a Philips PW1820 θ - 2θ goniometer. A 0.5° scatter slit and a 0.2° receiving slit were used during all the acquisitions.

|| AFM images were recorded in air with a NanoScope III (Digital Instruments Inc.) in the constant-force mode on the as-deposited samples. The detection scheme of this instrument is based on the laser beam deflection of a microfabricated Si_3N_4 cantilever (spring constant $0.58\ \text{N m}^{-1}$, scan rate $8.72\ \text{Hz}$) with an integrated Si_3N_4 pyramidal tip and subsequent detection by means of a split photo diode.

** X-Ray photoelectron spectroscopy depth profiles were obtained with a PHI5600 ESCA/SAM monochromator system obtaining X-ray photoelectron spectra ($\text{Al-K}\alpha = 1486.6\ \text{eV}$), anode voltage $14\ \text{kV}$, power setting $350\ \text{W}$ for the energy ranges in which the main photoemission processes for the elements of interest occur (30 second bursts of Ar^+ sputtering, Ar^+ accelerator voltage $3\ \text{kV}$, ion current $0.5\ \text{nA}$, rastered area $3 \times 3\ \text{mm}$). The spectra were performed at a 45° takeoff angle with a pass energy of $23.58\ \text{eV}$ for the wide scans and $5.85\ \text{eV}$ for the narrow scans. The typical operating pressure was in the range 10^{-9} – 10^{-10} Torr. The XPS spectrometer was calibrated using the Ag $3d$ region of an etched Ag sheet. The separation between Ag $3d_{3/2}$ ($368.3\ \text{eV}$) and the Ag $3d_{1/2}$ was $6.00\ \text{eV}$. The energy resolution was $0.48\ \text{eV}$. The binding energy of the experimental spectra was calibrated on the basis of the most intense peak of the C $1s$ region at $284.5\ \text{eV}$.

†† Rutherford backscattering spectra were obtained using a $2\ \text{MeV He}^+$ beam (van de Graaff generator). The beam current was $8\ \text{nA}$ and the backscattering angle was 160° .

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