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Characterization of sol–gel surfaces for biomedical applications

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The aim of the present study was to characterize sol–gel derived titania coatings prepared by dipping. The surface characterization was carried out using X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF SIMS), combined with X-ray diffraction (XRD) and thermal analysis. Sol–gel derived titania surfaces mimicked the surface chemistry of the natural oxide layer found on commercial titanium implants. These surfaces could be used to develop an *in vitro* model of the osseointegration process. Similar analytical techniques were applied to apatite-like coatings and preliminary results suggest that hydroxyapatite coatings can be produced from a sol–gel route.

1. Introduction

Titanium implants were first introduced in the 1970s by Branemark [1]. They are used in the dental and maxillofacial fields with excellent clinical results. This success is due partly to their good biocompatibility with living tissues [2]. Tissue response to titanium also appears to be linked with the properties of titanium oxide at the titanium surface [3]. Bone tissue bonds with the surface oxide layer after implantation, a phenomenon known as osseointegration. Tengwall *et al.* [4] have proposed that an interaction between the titanium oxide and hydrogen peroxide released during the biological process could leave the implant surface with abundant OH groups, which may influence the biocompatibility of titanium. It is also known [5] that sol–gel derived titania films can induce the precipitation of hydroxyapatite from metastable calcium phosphate solutions.

It is the aim of the present study to characterize sol–gel derived titania and apatite-like coatings prepared by dipping as potential model surfaces for the study of interfacial reactions with the biological environment and to apply coatings to materials which are considered to be bioinert. Sol–gel titania coatings have been produced successfully [6, 7] but not as yet adequately analysed using surface analysis techniques such as XPS. In contrast apatite-like coatings produced by the sol–gel route have received very little attention [8, 9], although other methods such as plasma spraying have attracted much study [10].

Sol–gel technology is a low temperature method of preparing inorganic materials from chemical routes. The technique allows materials to be mixed on a molecular level in a solution before being brought out of solution, either as a colloidal gel or a polymerized macromolecular network, while still retaining solvent. The solvent can then be evaporated off to leave a solid with a high level of fine porosity. It is this high surface area and, therefore, surface free energy, that provides the driving force for densification at lower temperatures than conventional routes.

Molecular mixing can be achieved during the hydrolysis of metal alkoxides. An organic solvent, usually an alcohol, acts as a mutual solvent for the alkoxide precursor and the water necessary for hydrolysis. A gelatinous network of polymeric species (gel) forms which is allowed to dry before a thermal treatment, during which residual organics are driven off and a dense oxide layer forms. The advantages of using a sol–gel dip-coating technique are that it is independent of substrate shape, and control over surface properties such as composition, thickness, contaminant levels and topography can be achieved.

2. Materials and methods

2.1. Sol–gel coating procedures

The coating process for the preparation of alkoxy-derived TiO_2 coatings is described elsewhere [7]. In this study titanium (IV) isopropoxide in isopropanol in a 1: 1 molar ratio was hydrolyzed and converted to titanium oxide in the presence of atmospheric moisture. A stabilizing agent, diethanolamine, was used to prevent precipitation of titania for the sol. Glass cover slips were ultrasonically cleaned and rinsed in methanol and distilled water prior to being dipped in the Ti sol. TiO_2 coatings down to 30 nm thick were obtained using withdrawal speeds from 1.5 to 0.1 mm/s. Thinner coatings were prepared by increasing the molar ratio of isopropanol in the starting sol. Coated cover

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slips were fired in an air furnace at temperatures from 100 to 600 °C for 1 to 3 h.

The firing range for apatite-like coatings was extended up to 1200 °C. For these higher temperatures a different substrate was required and zirconia discs prepared by hot pressing were selected. Zirconia is traditionally thought of as a bioinert material but it has the required strength and toughness of a structural implant. The discs were polished down to 1200 grade silicon carbide paper on one side and 1 μm on the other prior to being dip coated. Sol–gel solutions were prepared by dissolving 1.7×10^{-2} mol of calcium acetate in either distilled water or ethanediol. 1×10^{-2} mol of the following phosphorus precursors were added to the calcium precursor solution; phosphoric acid, phosphorus pentoxide refluxed with 1-propanol, and triethyl phosphite. These molar ratios ensured that Ca and P were present in the same stoichiometry as that found in hydroxyapatite (i.e. $Ca/P = 1.67$). Withdrawal speeds up to 2.5 mm/s were employed in the coating procedure.

Powders were prepared from these solutions by vacuum drying at 100 °C to remove the liquid phase. The powders were then fired in air up to 1100 °C using a heating rate of 10 °C/min and a 30 min dwell at the firing temperature, followed by a furnace cool.

2.2. Surface analytical procedures

X-ray photoelectron spectra (XPS) were recorded on a VG Scientific spectrometer using MgK_α X-rays and a take-off angle of 30° with respect to the sample surface. In order to determine surface compositions from XPS data, accurate sensitivity factors (sfs) are required to convert peak area ratios into atomic percentage ratios. In this work the sfs of Ward and Wood [11] were employed. The quantification error allowed determination of atomic percentages to within 1%.

For the calcium phosphate films the Ca/P ratio was determined from the quantified data and compared to the theoretical value of 1.67 for hydroxyapatite.

Positive and negative secondary ion mass spectra were obtained using a VG Ionex ToF SIMS instrument with a pulsed gallium ion primary source.

TiO_2 samples for X-ray diffraction (XRD) were prepared on microscope slides using a multiple dipping/firing programme to increase the film thickness. In this instance a dip-rate of $U = 2.5$ mm/s was used. X-ray spectra were obtained on a Philips PW 1710 diffractometer using CoK_α radiation. Scans were performed at 40 kV and 30 mA and $2\theta = 15$ to 65° with a step size of 0.02° and a speed of 0.02°/s. Data analyses (background subtraction, smoothing, peak numbering, etc.) were carried out using Sietronics PW 1710 diffractometer automations software. The same conditions were used to examine the CaP powders.

Differential thermal analysis (DTA) was carried out in air on a Stanton Redcroft DTA 673-4 instrument using a heating rate of 10 °C/min up to a temperature of 600 °C for titania films and 1200 °C for CaP samples. The baseline calibration was determined using an alumina standard.

A Stanton Redcroft TG 770 Thermogravimetric analysis (TGA) instrument was used to obtain data on weight losses arising from heat treatment. The same heating conditions as in the DTA tests were employed.

Films were examined using reflected light microscopy under an Olympus BH-MPS optical microscope.

3. Results and discussion

3.1. Titania

DTA and TGA traces for the TiO_2 gel are shown in Fig. 1. The TGA plot shows that all weight losses are complete by 550 °C, at which temperature all the organics have been driven off. The DTA plot shows large exotherms at about 250 °C and 350 °C. These exothermic reactions correspond to the decomposition of residual organics and combustion of organic matter followed by formation of bonds through condensation and polymerization. The last exothermic peak finished at about 400 °C, indicating that this is the lowest temperature that could be used for firing. The coating colour is affected by the dwell time at the firing temperature. Films held for 3 h reached transparency at 400 °C compared to 500 °C for films fired for 1 h. It is likely that complete pyrolysis of the diethanolamine stabilizing agent can occur only if films are heated for a sufficient time (i.e. greater than 60 min).

The surface analysis of the titania coatings by XPS provides valuable chemical state information. The atomic concentrations of elements in titania coatings fired at the lower and upper temperature regimes in this study are given in Table I. XPS studies of commercially pure titanium [12] revealed that the surface had a C content of 43%, more than double the amount of the sol–gel surfaces. In addition, other elements (N, Ca, Na, S, P, Si, K and Pb) were detected at levels of less than 1%. A typical survey scan for a sol–gel titania surface shows that the dominant

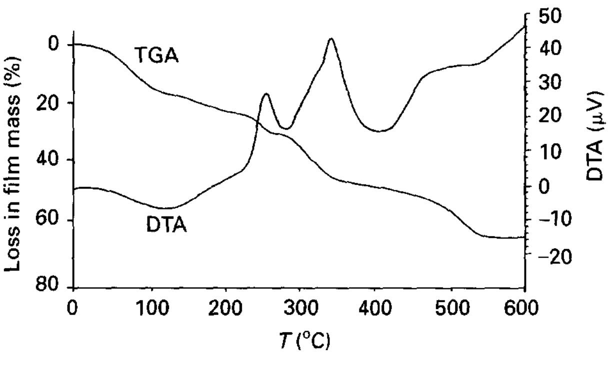

Figure 1 DTA/TGA trace for titania film heated to 600 °C.

TABLE I Atomic percentages of elements in titania coatings

Core line	Atomic percentage 100 °C fire, 3 h	Atomic percentage 600 °C fire, 3 h
C 1s	49.0	16.7
O 1s	32.8	57.1
Ti 2p 3/2	9.3	21.2
Na 1s	0	5.0
N 1s	8.9	0

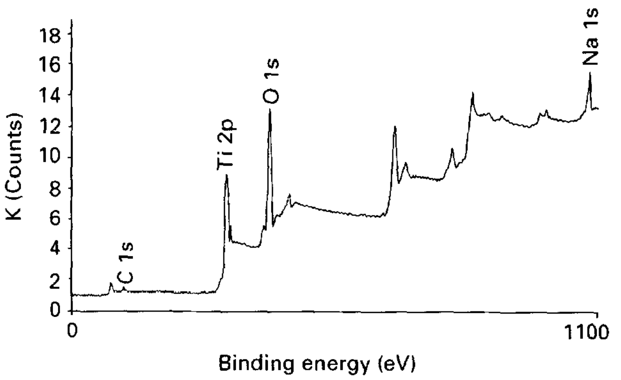

Figure 2 XPS survey scan for a titania film fired at 600 °C for 3 h.

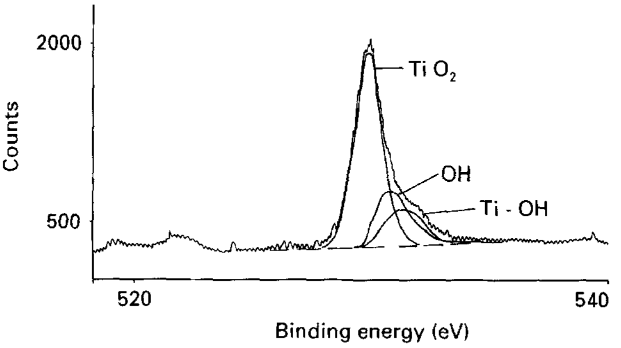

Figure 3 1s core line in a titania film fired at 600 °C for 3 h.

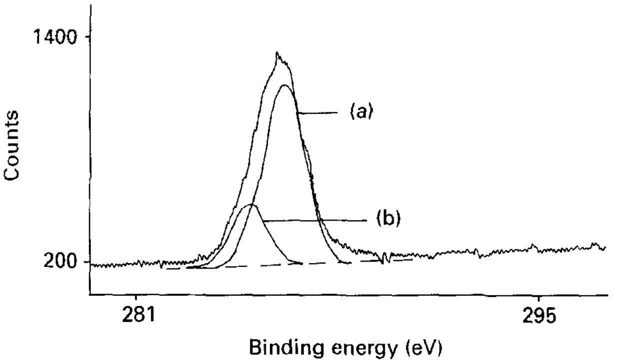

Figure 4 C 1s core line for a film fired at 100 °C for 3 h: (a) hydroxyl C–OH 74%; (b) hydrocarbon 26%.

signals are Ti, O and C with a weak contribution from Na arising from diffusion from the glass substrate at elevated temperatures (Fig. 2). A previous study of the surface chemistry of sol–gel prepared titania surfaces [13] indicated that for films fired at 600 °C the surface oxide is mainly titanium (IV) oxide. Further examination of the O 1s core line (Fig. 3) showed that the major peak at 530 eV could be assigned to oxygen of TiO_2 while the shoulder at higher binding energy was typical of physisorption of (OH) and chemisorbed water (i.e. TiOH). The fitting of the C 1s core line using Gaussian model peaks showed that at 600 °C only one carbon environment was present, i.e. hydrocarbon C–C or C–H. This was in contrast to films fired at lower temperatures, which retained significant organic character, as seen from the presence of a hydroxyl (C–OH) peak in the C 1s core line for a film treated at 100 °C (Fig. 4). A study by Shirkhanzadeh [14] reports the preparation of a titania film by an electrochemical method. XPS analysis of these coatings indicated that rather than a single C environment, the electrochemically prepared films exhibited four distinct carbon environments. Similarly, the carbon contamination on commercially pure titanium existed in four discrete environments. The majority was found to be hydrocarbon but hydroxyl (C–O), carbonyl (C = O) and carboxyl (O–C = O) environments were also detected. The absence of complex carbon contamination of the sol–gel prepared surface suggests that it is chemically cleaner than that of commercially pure titanium.

SIMS was used to probe the surface of the titania films. Because different ions have different ionization probabilities, SIMS is not a directly quantifiable technique, but lends itself more to elucidation of structural information. In the positive ion spectra the major ions diagnostic of TiO_2, were detected. These ions are documented in Table II. Several ions diagnostic of hydrocarbon contamination were detected in the positive and negative ion spectra, most notably at $m/z = 13$ (CH^-) and $m/z = 41$ $(C_3H_5^+)$. A series of fragment ions at $m/z = 15, 29$ and 43 correspond to loss of $CH_3(CH_2)_n$, where $n = 0$ to 2 [15]. These ions are characteristic of hydrocarbon fragments from isopropanol and the isopropyl chain groups in titanium isopropoxide. A low count rate at $m/z = 32$ (O^{2-}) is indicative of the film structure comprising a tetrahedral network of Ti–O linkages rather than discrete TiO_2 units.

Crack-free titania coatings were produced across the whole firing range of employing a withdrawal rate from the sol of 0.1 mm/s. This resulted in a film approximately 30 nm thick. This is an order of magnitude thicker than the natural oxide layer found on commercial titanium implants [12]. The coating thickness can be reduced tenfold by increasing the molar concentration of isopropanol in the original sol (Fig. 5). The lower limit for the coating thickness was determined from the sampling depth equation [16]:

$$\text{s.d.} = 3\lambda \sin \theta$$

where λ is the electron escape depth and θ is the take-off angle.

TABLE II Ion fragments diagnostic of TiO_2, as detected by SIMS

m/z	48	64	65	80	81	97
Ion	Ti^+	TiO^+	$TiOH^+$	TiO_2^-	$TiO.OH^+$	TiO_2OH^-

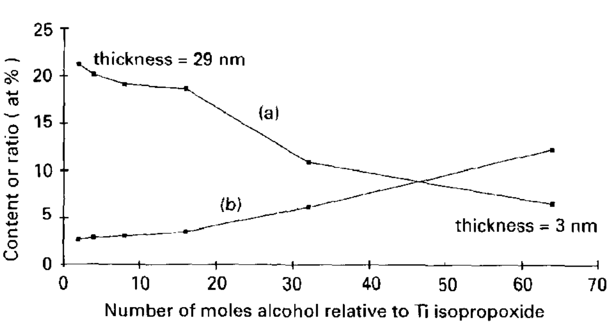

Figure 5 Graph showing (a) Ti content and (b) O/Ti ratio varying with number of moles isopropanol relative to Ti alkoxide in the starting sol.

At the highest molar concentration of alcohol (64 moles alcohol to 1 mole titanium isopropoxide) a Si 1s signal from the glass substrate was detected by XPS. Taking the escape depth of Si to be 2 nm gave a minimum film thickness of 3 nm. There is a compromise between reducing the film thickness to approach that of the natural oxide layer on a Ti implant and decreasing the Ti/O ratio from the ideal value of 2. At present it is unclear what effect the altered Ti/O ratio of the thinner films has on their biocompatibility.

XRD patterns were obtained from multiply dipped films of titania at temperatures from 100 to 600 °C (Fig. 6). The as-dipped coatings were amorphous but crystallized to anatase above 400 °C. The patterns in Fig. 6e and f show a significant orientation along [1 0 1] direction, with the degree of crystallization increasing with firing temperature. Electrochemically prepared films [14] showed similar crystallization behaviour but the conversion temperature was somewhat higher, 550 °C.

3.2. Apatite-like coatings

The Ca/P ratio of films prepared from calcium and phosphorus was determined by XPS. Table III indicates that samples prepared from calcium acetate with P_2O_5 in alcohol and phosphoric acid were calcium deficient, having Ca/P ratios significantly less than one. When an organic solvent (ethanediol) was used with a phosphoric acid precursor the Ca/P ratio was increased slightly but calcium deficiency was still significant. When triethyl phosphite was used as a P precursor the Ca/P ratios obtained approached the theoretical value of 1.67 for hydroxyapatite, taking into account the error in quantifying atomic percentages from the XPS data ($\sim 1\%$). In contrast to the case of phosphoric acid, when ethanediol was used as a solvent for triethyl phosphite. the Ca/P ratio dropped significantly, indicating that this solvent was not ideal for this system.

Although XPS is a powerful tool for evaluating atomic percentages and atomic ratios, it is not ideally suited to chemical phase determination. XRD of powders prepared from calcium acetate solutions indicated that the desired hydroxyapatite phase was not formed at any firing temperature when the P precursor was phosphoric acid or phosphorus pentoxide refluxed with alcohol. Only with triethyl phosphite as the precursor was the crystalline phase of HA detected. The DTA trace for this system (Fig. 7) shows an endotherm at about 210 °C indicating escape of acetate. The XRD plot at this temperature (Fig. 8a) shows an essentially amorphous powder. Large exothermic effects are seen at temperatures in excess of 500 °C and the corresponding XRD trace shows that in addition to the oxidation of organic species, the exotherm can be attributed to the formation of calcium carbonate and HA. The exotherm at about 580 °C can be assigned to carbonate hydroxyapatite formation. The XRD pattern is similar to that of commercial hydroxyapatite, with one extraneous peak at $2\theta = 44$ degrees. The last exotherm ends at approximately 900 °C and the calcined product now has a well-defined crystalline HA structure. When calcium acetate in ethanediol was used rather than an aqueous solution the resulting HA diffraction pattern showed that the hydroxyapatite phase formed was impure, with numerous peaks infringing on the pure apatite pattern (Fig. 9). These peaks can be attributed to α and β tricalcium phosphate (α, β $Ca_3(PO_4)_2$), TCP

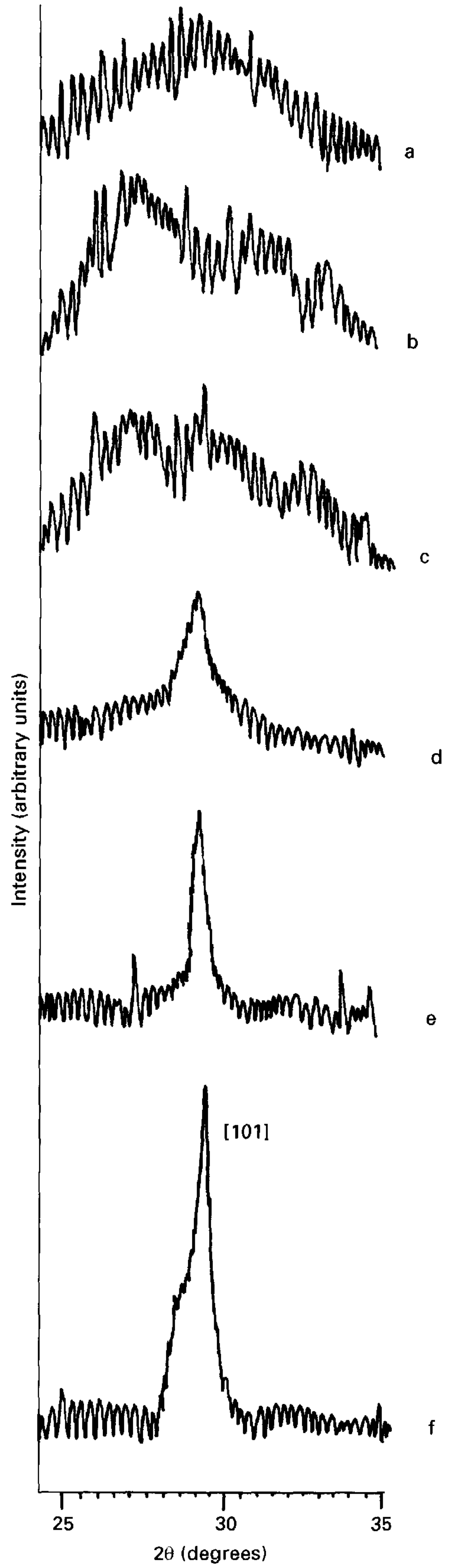

Figure 6 X-ray diffraction patterns for titania films fired at (a) 100 °C, (b) 200 °C, (c) 300 °C, (d) 400 °C, (e) 500 °C and (f) 600 °C.

TABLE III Ca/P ratios in calcium phosphate coatings prepared from calcium acetate and fired at different temperatures

P precursor	Ca/P at 100 °C	Ca/P at 800 °C	Ca/P at 1000 °C
H_3PO_4	0.6	0.6	0.52
H_3PO_4 + ethanediol	0.76	0.72	0.75
P_2O_5 in 1-propanol	0.43	0.53	0.34
$P(OC_2H_5)_3$	1.49	1.58	1.62
$P(OC_2H_5)_3$ + ethanediol	1.03	1.06	1.09

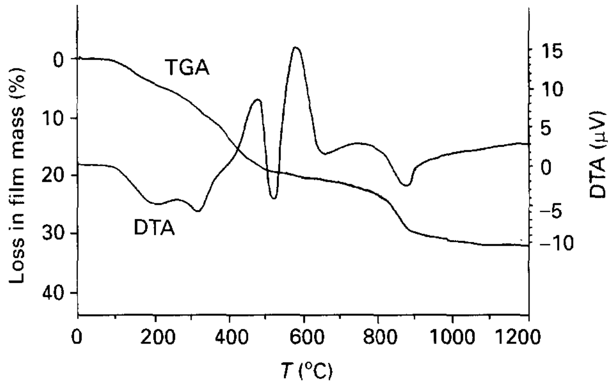

Figure 7 DTA/TGA trace for a powder prepared from aqueous calcium acetate with triethyl phosphite.

and tetracalcium phosphate ($Ca_4P_2O_9$), TP. The pure hydroxyapatite structure incorporates two moles of water–$Ca_{10}(PO_4)_6(OH)_2$. The preparation from aqueous calcium acetate introduces H_2O into the system but when ethanediol is used there is no provision for incorporating the water fraction. The only water present in this latter system arises from the atmospheric moisture in contact with the film immediately after the dipping process.

Powders prepared at temperatures up to 800 °C were grey in colour, suggesting that organic species were still present. These observations are consistent with DTA traces which suggest that reactions are still taking place at this temperature. Weight loss is complete at about 950 °C, indicating that all organics have been expelled at this temperature.

Wetting of the substrate is of major importance when preparing sol–gel films. Calcium acetate solutions had poor wetting characteristics after firing. Phosphorus pentoxide refluxed in alcohol was particularly poor, owing perhaps to the volatility of this P precursor. After removal from the coating solution, films prepared from calcium acetate with triethyl phosphite wetted the zirconia substrate and were seen to be crack free for withdrawal speeds up to 2.5 mm/s (Fig. 10). After firing at temperatures above 200 °C excessive shrinking and beading was apparent (Fig. 11) and a patchy layer was evident at the base of the zirconia disc where the liquid had gathered and subsequently been heat treated. Fig. 12 indicates that after firing, where sections of film had remained intact, they were free from cracks. The interference fringes seen in Fig. 12 show that film shrinkage and beading result in a coating of non-uniform thickness. These interference fringes seen in the film under ordinary light indicate that the film thickness is of the order of the wavelength of light. For this system to be successful the surface chemistry must be investigated. The

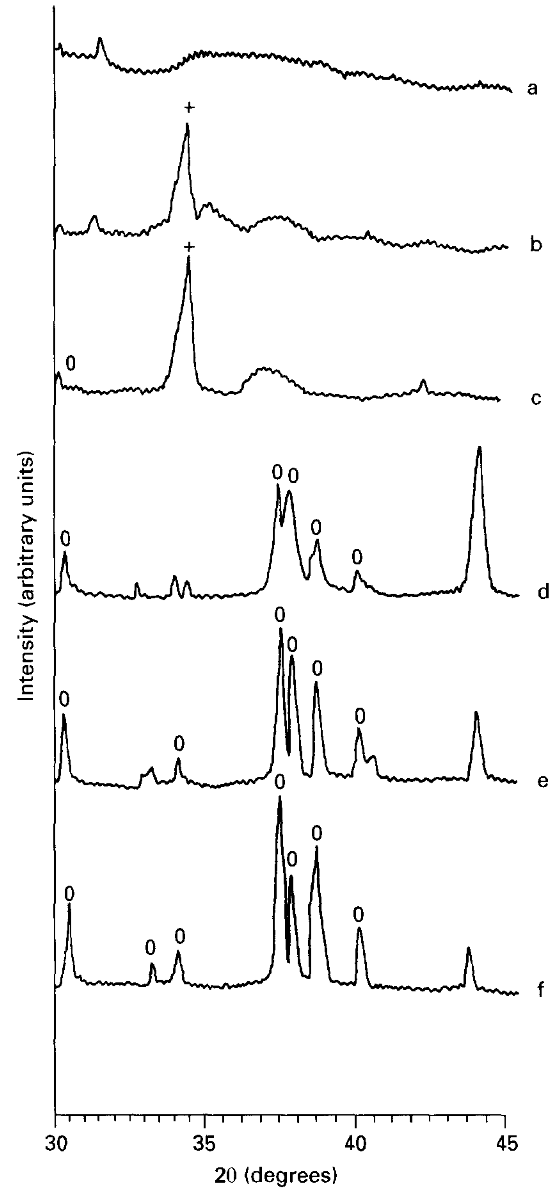

Figure 8 X-ray diffraction patterns for powder prepared from aqueous calcium acetate with triethyl phosphite heated at (a) 200 °C, (b) 400 °C, (c) 500 °C, (d) 600 °C, (e) 800 °C and (f) 900 °C: ○ HA; + $CaCO_3$.

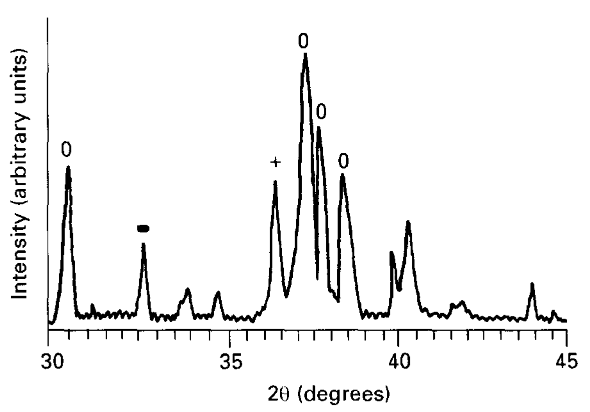

Figure 9 X-ray diffraction pattern for calcium acetate in ethanediol + triethyl phosphite heated to 900 °C: ○ HA; + TCP; – TP.

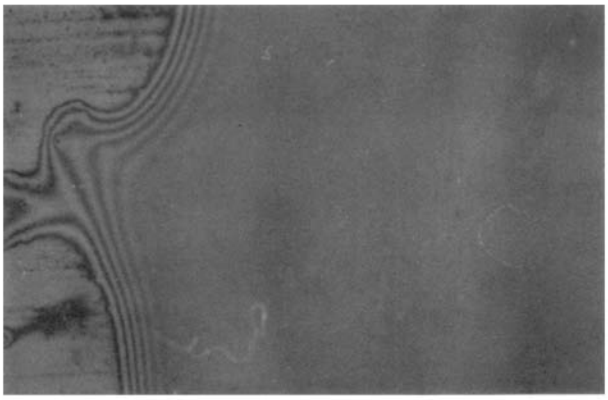

Figure 10 As-dipped film prepared from calcium acetate + triethyl phosphite.

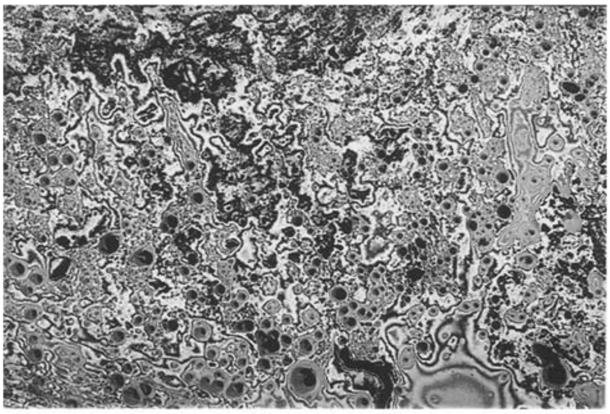

Figure 11 Calcium phosphate film after firing at 1000 °C, showing film shrinkage.

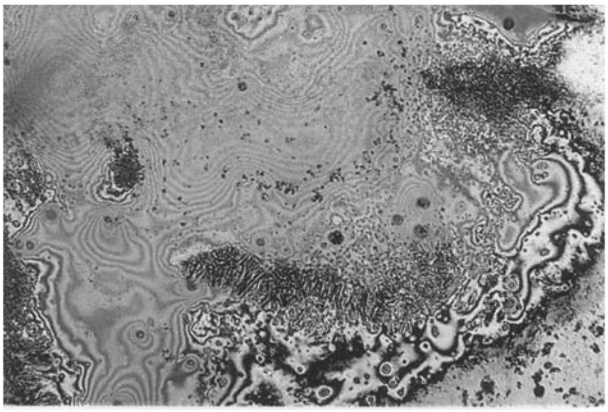

Figure 12 Section of fired film showing a crack-free coating of non-uniform thickness.

wetting problems may be linked with surface energy criteria or solution viscosity. Some of these wetting problems were overcome by utilizing a multiple dipping technique but this method is not totally satisfactory since control over the coating thickness and surface quality are lost.

4. Conclusions

The data reported show that it is possible to mimic the surface chemistry of commercial titanium implants using a sol–gel technique. Firing at 600 °C for 3 h produced a coating predominantly inorganic in character with the minimum amount of organic residues. The abundance of surface hydroxyl groups on the surface mean that sol–gel prepared titania may induce apatite nucleation from simulated body fluids. The intention is to use these films as the basis for an *in vitro* study of the osseointegration process. Apatite-like coatings have been applied to zirconia discs with some success. Wetting of the substrate requires improvement but X-ray diffraction showed that crystalline hydroxyapatite can be obtained at temperatures below 1000 °C from a sol consisting of aqueous calcium acetate and triethyl phosphite. Further work will concentrate on improving substrate wetting and carrying out *in vitro* studies to determine the bioactive properties of the hydroxyapatite coatings.

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