Chapter-4
ELECTRODEPOSITION OF CALCIUM PHOSPHATE COATINGS ON STAINLESS STEEL SUBSTRATES

Abstract

Section-A

Cathodic reduction of an aqueous solution containing dissolved calcium and phosphate ions results in the deposition of micrometer thick CaHPO₄·2H₂O (dicalcium phosphate dihydrate) coatings on stainless steel substrates. The coating obtained at a low deposition current (8 mA cm⁻²) comprises lath-like crystallites oriented along 020. The 020 crystal planes are nonpolar and have a low surface energy. At high deposition currents, platelets oriented along 121 are deposited. CaHPO₄·2H₂O is an important precursor to the nucleation of hydroxyapatite, the inorganic component of bones. Differently oriented CaHPO₄·2H₂O coatings transform to hydroxyapatite with different kinetics, the transformation being more facile when the coating is oriented along 121. These observations have implications for the development of electrodeposited biocompatible coatings for metal endoprostheses for medical applications.

Section-B

Calcium hydroxyapatite coatings were obtained by cathodic reduction of Ca-L (L = EDTA, Lactic acid) complex at different temperatures (65-85°C) and different Ca to ligand ratios. Reduction of Ca-EDTA complex at 65 °C gives unoriented coatings and the coatings obtained at 85°C show 002 orientation. The extent of orientation decreases with increasing calcium concentration in the bath. The 002 orientation was also observed when the Ca-Lactic acid complex was reduced at 65°C and the extent of orientation increases as the deposition temperature increases. This shows that orientation of hydroxyapatite coatings depends on the stability of the complex, degree of supersaturation and the deposition temperature.
Section-A

Electrodeposition of dicalcium phosphate dihydrate coatings on stainless steel substrates

4.1 Introduction

Calcium phosphate crystallizes in various forms, such as dicalcium phosphate dihydrate (CaHPO₄·2H₂O, DCPD), dicalcium phosphate anhydrous (CaHPO₄, DCPA), tricalcium phosphate (Ca₃(PO₄)₂, TCP), octacalcium phosphate (Ca₈(HPO₄)₂(PO₄)₄·5H₂O, OCP), amorphous calcium phosphate (ACP) and hydroxyapatite (Ca₁₀(PO₄)₆(OH)₂, HA). Among all the calcium phosphate phases, hydroxyapatite is the thermodynamically most stable phase. The formation of different phases depends upon the Ca/P molar ratio, pH and temperature of synthesis.¹

Calcium phosphate phases are important bio-inorganic materials involved in the biomineralization of bones and teeth.² They are also used as tooth filling cements³ and as biocompatible coatings for metal endoprostheses.⁴

Among the various calcium phosphates, DCPD is important for the following reasons: (1) DCPD is an acidic calcium phosphate and consequently has high solubility under physiological conditions. Thereby, it is an important precursor to the crystallization of hydroxyapatite, the inorganic component of the bone material.⁵ (2) DCPD is also found in pathological calcification as in dental calculi, crystalluria and urinary stones.⁶⁻⁸ (3) In therapeutics, DCPD is used in calcium phosphate cements⁹ and as an intermediate for tooth remineralization.¹⁰ (4) DCPD also has technological applications as a flame retardant.¹¹

DCPD crystallizes below pH 6.0 with monoclinic symmetry.¹² The unit cell consists of alternating bilayers stacked along the b-crystallographic axis. One layer consists of calcium and hydrogenphosphate ions and the other layer contains water molecules. The calcium ions are octacoordinated by six oxygen atoms of the anions and by two oxygen atoms of the water molecules.¹³

For biomedical applications it is important to make calcium phosphate coatings on metal surfaces. Many techniques are reported in the literature for the fabrication of calcium phosphate coatings on metal surfaces, such as rf sputtering,¹⁴ chemical vapor deposition¹⁵ and chemical spraying.¹⁶ These methods require the prior synthesis of the
desired material, high vacuum chamber, high power laser or electron beam source. They are cost and energy intensive and one may not get the desired composition in the coating.

Electrodeposition\textsuperscript{17,18} is a simple and low temperature technique for the fabrication of coatings of diverse materials on metal surfaces. By using this method it is possible to fabricate coatings on irregular objects, control the morphology and orientation by varying the deposition current, potential and bath composition.

In this section, we report the electrodeposition of DCPD (CaHPO\textsubscript{4}-2H\textsubscript{2}O) coatings on stainless steel substrates. A switch in the crystal orientation of the deposit was observed when the deposition current was changed. Differently oriented DCPD coatings were found to transform into hydroxyapatite with different kinetics. Based on the surface energies of the different crystal faces of DCPD and the observed morphological changes, we suggest the transformation occurs by a dissolution-reprecipitation mechanism.

4.2 Experimental

A diammonium hydrogenphosphate solution (0.60 M, 50 mL) was added to a standard (1 M) calcium nitrate solution (50 mL). The white precipitate formed was dissolved using dilute nitric acid and the clear solution was diluted to obtain a stock solution 0.2 M in Ca\textsuperscript{2+} ([Ca]/[P] = 1.67). The pH of the stock solution was 2.4. All the solutions were prepared using ion-exchanged Type-I water (Milli-Q Academic water purification system, specific resistance 18.2 M\textohm cm).

A stainless steel flag (area 4.5 cm\textsuperscript{2}) was used as cathode and a Pt mesh (28 cm\textsuperscript{2} geometric area) was used as the counter electrode. The depositions were carried out galvanostatically (current density 8-12 mA cm\textsuperscript{-2}, t 60 min) using CHI Model 408A galvanostat/potentiostat. The deposition potentials were measured with respect to a saturated calomel electrode. During electrodeposition, the temperature of the bath was maintained at 45°C (IKA ETS-D5 Heater). After deposition, the coatings were rinsed with Type-I water and dried at 65°C. Prior to electrodeposition, the working electrode was electrochemically polished as explained elsewhere.\textsuperscript{19} At least two coatings were prepared under each condition to verify the reproducibility of the observed effects.
CaHPO$_4$.2H$_2$O $\rightarrow$ hydroxyapatite transformation was carried out by ageing the as-deposited coatings in 2 M sodium hydroxide at 60-85°C for 6-18 h. After ageing, the coatings were rinsed with Type-I water and dried at 65°C.

All the coatings were characterized by X-ray diffraction (XRD), by mounting the electrode directly on a Bruker aXS Model D8 Advance powder X-ray diffractometer (Cu Kα source $\lambda = 1.5418$ Å). XRD profiles were fit by the Rietveld method (Fullprof Suite), using the published structure of CaHPO$_4$.2H$_2$O (ICSD No. CC 16132) ($I$1$a$1, $a = 5.812$ Å, $b = 15.180$ Å, $c = 6.239$ Å, $\beta = 116.43^\circ$). The quality of the fit was judged from the R values and also by an examination of the difference profile. The observation of systematic residual intensities in the difference profile at positions corresponding to the different Bragg reflections is indicative of oriented crystallization. In such case, the Rietveld refinement was repeated by the inclusion of March function parameters to account for orientation. The March function has two refinable parameters, $G_1$ and $G_2$. Of importance in the present context is $G_2$. $G_2 = 0$ corresponds to a fully oriented coating, while $G_2 = 1$ to a coating without any preferred orientation.

IR spectra were recorded using a Bruker Alpha-T FTIR spectrometer (Diamond crystal ATR mode, resolution 4 cm$^{-1}$, 400-4000 cm$^{-1}$). Surface morphologies were studied using a scanning electron microscope (JEOL Model JSM 6490LV microscope, operating voltage 15 kV) by mounting the as-prepared coating on conducting carbon tape and sputter coating with Pt to improve conductivity.

4.3 Results and Discussion

On passing current in a bath containing calcium and hydrogenphosphate ions, a white calcium phosphate film is seen to form within 5 minutes. While the bulk pH is controlled by acidification of the bath to suppress the chemical precipitation of calcium phosphate phases, the pH at the surface of the cathode is higher than the bulk pH$^{20}$ and is determined by the various electrochemical reactions taking place close to it. The high pH generally causes the deposition of metal hydroxide or oxide coatings on the cathode.$^{21}$ However, in the presence of phosphate ions in the bath, metal phosphates are formed owing of their lower solubility than metal hydroxides.$^{22}$
The reactions that take place at the cathode during the electrodeposition of CaHPO$_4$·2H$_2$O are:

1. Electrogeneration of base by electrolysis of water and nitrate reduction

   \[ 2 \text{H}_2\text{O} + 2 \text{e}^- \rightarrow 2 \text{OH}^- + \text{H}_2 \]
   \[ \text{NO}_3^- + 2 \text{e}^- + \text{H}_2\text{O} \rightarrow 2 \text{OH}^- + \text{NO}_2^- \]

2. Phosphate ion speciation depending upon the pH

   \[ \text{H}_2\text{PO}_4^- + \text{OH}^- \rightarrow \text{HPO}_4^{2-} + \text{H}_2\text{O} \]

3. Formation of CaHPO$_4$·2H$_2$O

   \[ \text{Ca}^{2+} + \text{HPO}_4^{2-} + 2 \text{H}_2\text{O} \rightarrow \text{CaHPO}_4·2\text{H}_2\text{O} \]

The different hydrogenphosphates are easily distinguished by their characteristic IR spectra, especially in the OH stretching region. There are four vibrations in the range 3600-3100 cm$^{-1}$ (Fig. 4.1a), which show the presence of two kinds of water molecules. Lecomte and co-workers$^{23}$ have assigned the high wave number peaks to bound water molecules and low wave number peaks to the free water molecules. On the other hand, Petrov et al.$^{24}$ have assigned the higher wave number peaks to loosely bound water and low wave number peaks to water molecules directly bonded to calcium atoms. The absorptions in the range 1250-500 cm$^{-1}$ correspond to HPO$_4^{2-}$.

![Fig. 4.1 IR spectra of (a) DCPD and (b) hydroxyapatite coatings.](image-url)
X-ray diffraction was used for identification of the electrodeposited solid. The XRD pattern of the as-deposited coating obtained when the deposition current was 8 mA cm\(^{-2}\) is shown in Fig. 4.2. Sharp Bragg reflections are observed at d-spacings corresponding to the DCPD phase as reported in JCPDS database (PDF: 72-0713). However, the observed relative intensities of the different reflections do not match with those reported. On performing a Rietveld fit of the observed profile, residual intensity was seen in the difference profile at the 2θ value corresponding to the 020 plane. Such residual intensities are generally due to oriented growth. The refinement was repeated by incorporating March function parameters to account for preferred orientation along this direction (Table 4.1). The resultant fit was satisfactory and the difference profile was a smooth function.

![Graph showing XRD patterns](image)

**Fig. 4.2** XRD pattern of (a) DCPD coating obtained at 8 mA cm\(^{-2}\) deposition current compared with (b) the calculated XRD profile incorporating the effect of orientation and (c) is the corresponding difference profile. (d) and (e) are the calculated XRD profile and difference profile, respectively, obtained before the incorporation of orientation effects.
The XRD pattern of a CaHPO₄·2H₂O coating obtained when the deposition current was 12 mA cm⁻² is shown in Fig. 4.3. In this pattern the peak corresponding to the 12\( \bar{1} \) reflection is the strongest of all the observed reflections. In this case, Rietveld fit of the observed profile shows residual intensity in the difference profile at 2\( \theta \) value corresponding to the (12\( \bar{1} \)) plane. After repeating the refinement with orientation parameters (see Table 4.1) the difference profile was a smooth function.

![XRD pattern](https://example.com/xrd-pattern)

**Fig. 4.3** XRD pattern of (a) DCPD coating obtained at 12 mA cm⁻² deposition current compared with (b) the calculated XRD profile incorporating the effect of orientation and (c) is the corresponding difference profile. (d) and (e) are the calculated XRD profile and difference profile, respectively, obtained before the incorporation of orientation effects.
Morphologies of all the coatings were examined by scanning electron microscopy (SEM). The SEM images of the 020 oriented coatings (Fig. 4.4a, b) show laths having a length of several micrometers. Fig. 4.4c shows the structure of the DCPD which consists of bilayer arrangement of calcium, hydrogenphosphate and water molecules. The 020 plane ends with a layer of water molecules. Consequently, the 020 plane is non-polar. In general non-polar crystal planes have a low surface energy and crystal growth along the normal does not lead to significant energy gains as bonding is weak. On the contrary strong ionic-covalent bonding leads to in-plane growth as accretion of atoms to the plane edges leads to large energy gains. The resultant crystallites are found to terminate at the 020 crystal planes leading to the lath-like morphology. Fig. 4.4d is a schematic of one such lath.

Table 4. 1 March function parameters obtained from Rietveld fits of the observed XRD profiles of DCPD coatings.

<table>
<thead>
<tr>
<th>Deposition current (mA cm⁻²)</th>
<th>Orientation</th>
<th>March function parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>020</td>
<td>G₁ 0.43  G₂ 0.62</td>
</tr>
<tr>
<td>12</td>
<td>12T</td>
<td>G₁ 0.50  G₂ 0.73</td>
</tr>
</tbody>
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Fig. 4.4 SEM images of 020 oriented DCPD coatings obtained at (a) low and (b) high magnifications respectively. (c) Crystal structure of the DCPD and (d) the schematic of a lath-like crystallite facetted by the 020 crystal plane.
The scanning electron microscopy images (Fig. 4.5) of a 12I oriented coating show platelet-like crystallites stacked one above the other. These stacks are inclined to the substrate surface. The stacks are oriented in different directions to yield clusters. These clusters are seen together with lath-like crystallites.

Fig. 4.5 SEM images of 12I oriented DCPD coatings obtained at (a) low and (b) high magnifications respectively. (c) A schematic of the unit cell of DCPD showing the 12I crystal plane. The axes are labeled with respect to monoclinic symmetry. Labels in parentheses correspond to the pseudo-hexagonal symmetry. (d) The pseudo-hexagonal platelets tilted to produce a 12I out of plane orientation.
At high currents the deposition process enters the regime of kinetic control, leading to growth of planes other than the thermodynamically stable 020 plane. The value of the crystallographic angle, β, of DCPD is 116.43° and is close to the hexagonal value of 120°. Consequently a pseudo-hexagonal symmetry can be visualized in the DCPD crystal, bounded by the \( \{hk0\} \) planes \( \{h, k = 0, \pm 1\} \). Crystal growth in the \( a-b \) plane of the pseudo hexagonal lattice \( \langle a-c \rangle \) plane of the monoclinic crystal) leads to crystallites with a hexagonal platelet morphology. The \( \langle 12\bar{1}\rangle_m \) \( \langle m: \text{monoclinic} \rangle \) plane is inclined to the \( [001]_h \) \( \langle h: \text{pseudo-hexagonal} \rangle \) as shown in Fig. 4.5c. When the platelets are inclined with respect to the substrate, the \( [12\bar{1}] \) is normal to the substrate, resulting in the \( 12\bar{1} \) out of plane orientation for the coating (Fig. 4.5d). Further the high rate of deposition also causes secondary nucleation generating stacks of crystallites.

**DCPD → HA transformation**

DCPD coatings were aged in alkali at different temperatures for different lengths of time to transform them into the hydroxyapatite phase. The reaction is

\[
5 \text{CaHPO}_4\cdot2\text{H}_2\text{O} + 6 \text{OH}^- \rightarrow \text{Ca}_9(\text{PO}_4)_3(\text{OH}) + 2 \text{PO}_4^{3-} + 15 \text{H}_2\text{O}
\]

However, the transformation kinetics were different in differently oriented coatings. The coating with 020 orientation was comparatively more stable and resistant to ageing. A complete transformation could not be affected below 85°C. At lower temperatures (60°C) and various ageing times (6-18 h), the Bragg reflections of the DCPD phase are absent, but reflections due to HA are not well defined (Fig. 4.6a, b). At this stage, the morphology of the coating is the same as that of the precursor DCPD phase and laths similar to those in Fig. 4.4 are seen (Fig. 4.6d). The sum total of the evidence points to an incomplete transformation. At 85°C the transformation is complete even at short ageing times (6 h) and the corresponding XRD pattern (Fig. 4.6c) is indexed to hexagonal HAP \( a = 9.352 \text{ Å }; \ c = 6.882 \text{ Å } \). The morphology has completely changed. A continuous covering of the substrate is observed, such a morphology is obtained by the merging of parallely oriented laths across their edges. Residual striations can still be seen in certain regions of the coatings (Fig. 4.6e).

The formation of the hydroxyapatite phase could also be seen in the IR spectra (Fig. 4.1b), which shows the disappearance of the vibrations due hydrogenphosphate and
the appearance of a single broad vibration due to the tetrahedral orthophosphate ion. The OH stretching region also shows changes expected of this transformation.

Fig. 4.6 XRD patterns and SEM images of hydroxyapatite coatings obtained from 020 oriented DCPD coatings aged at (a, d) 60°C for 6 h, (b) 60°C for 18 h and (c, e) 85°C for 6 h.
The DCPD coating with 12I orientation undergoes a facile transformation to HA at 60°C (duration 6 h) itself (Fig. 4.7). The X-ray pattern shows all the reflections expected of hydroxyapatite and in this case the platelets of the precursor coating are seen to merge at their edges to create a mosaic pattern that covers the substrate surface completely.

Fig. 4.7 XRD pattern and SEM image of a hydroxyapatite coating obtained from a 12I oriented DCPD coating aged at 60°C for 6 h.
4.4 Conclusions

In conclusion, we report the one step electrodeposition of dicalcium phosphate dihydrate (DCPD) coatings on stainless steel substrates by cathodic electrogeneration of base. The coatings grow in two preferred directions- 020 and 12\(\bar{1}\) depending upon the deposition current. The biochemical importance of DCPD arises on account of its ability to transform into hydroxyapatite, the inorganic component of bones. The DCPD coating oriented along 12\(\bar{1}\) transforms to hydroxyapatite in a very facile manner at a lower temperature (60\(^\circ\)C) and shorter ageing time (< 6 h) compared to the coating oriented along 020. This observation is in keeping with the lower surface energy and higher thermodynamic stability of the 020 crystal plane of DCPD. The low surface energy of the 020 plane is on account of its nonpolar nature which inhibits interaction with the polar solvent.
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Section-B

Oriented crystallization of calcium hydroxyapatite coatings in presence of complexing agents

4.5 Introduction

Hydroxyapatite (HA), \( \text{Ca}_5(\text{PO}_4)_3\text{OH} \), is the thermodynamically most stable phase among the various calcium phosphate phases.\(^1\) Hydroxyapatite is one of the important phases of interest among the various calcium phosphate based bioceramics, because it is the main constituent of bone and teeth\(^2\) and it can be effectively used as a biocompatible coating on metal substrates for implant applications.\(^3\) It is also important in catalysis, as fluorescence carrier, in the fertilizer industry, and in chromatography.\(^4\-\^6\) Hydroxyapatite shows very good substitution chemistry.\(^7,\^8\) The hydroxyl ion can be substituted by ions like F/Cl to get flour/chlorapatite. Calcium can be substituted by cations such as Sr, Ba, Ni, Co, and Pb. PO\(_4^{3-}\) ion can be substituted by the other tetrahedral anions such as arsenate and chromate.

For implant applications it is important to make hydroxyapatite coatings on metal surfaces. Various techniques are reported for the fabrication of hydroxyapatite coatings on metal surfaces, such as plasma spraying,\(^9\) pulsed laser deposition,\(^10\) sol gel process\(^11\) and electrodeposition.\(^12\-\^15\) Among all the techniques, electrodeposition is a convenient soft chemical technique to obtain biocompatible coatings on various substrates of different shapes and exercise facile control over thickness and composition of the coating.

In the earlier section, we obtained poorly ordered HA coatings through a two step route involving the electrochemical deposition of DCPD followed by chemical transformation to HA. Further the bath used comprised free Ca\(^{2+}\) ions, which precipitates on the addition of the phosphate source. The precipitate has to be redissolved by acidification of the bath.

In this Section we report a one-step electrodeposition of oriented hydroxyapatite coatings on stainless steel substrates in presence of complexing agents at different temperatures and Ca to ligand ratios.
4.6 Experimental

Hydroxyapatite coatings were made by cathodic reduction of mixed Ca(NO₃)₂, ligand and diammonium hydrogenphosphate solution. A typical bath was prepared by adding equal volumes (25 mL) of stock solutions of calcium nitrate (0.05-0.1 M), ligand (0.025-0.05 M) and diammonium hydrogenphosphate (0.03-0.06 M) in that order. The resultant mix was a clear solution with pH = 3.5-3.6. Two identical baths were prepared under each condition. One was aged to check for bath stability. The other was used for electrochemical deposition. All the solutions were prepared using ion-exchanged Type-I water (Milli-Q Academic water purification system, specific resistance 18.2 Megaohm cm).

A stainless steel flag (area 4.5 cm²) was used as cathode and a Pt mesh (28 cm² geometric area) was used as the counter electrode. The depositions were carried out galvanostatically (current density 15 mA cm⁻², t 10-30 min) using CHI Model 408A galvanostat/potentiostat. The deposition potentials were measured with respect to a saturated calomel electrode. During electrodeposition, the temperature of the bath was maintained at 65-85°C (IKA ETS-D5 Heater). After deposition, the coatings were rinsed with Type-I water and dried at 65°C. Prior to electrodeposition, the working electrode was electrochemically polished as explained elsewhere.¹⁶

All the coatings were characterized by X-ray diffraction (XRD), by mounting the electrode directly on a Bruker aXS Model D8 Advance powder X-ray diffractometer (Cu Kα source λ = 1.5418 Å). IR spectra were recorded using a Bruker Alpha-T FTIR spectrometer (Diamond crystal ATR mode, resolution 4 cm⁻¹, 400-4000 cm⁻¹). Surface morphologies were studied using a scanning electron microscope (JEOL Model JSM 6490LV microscope, operating voltage 15 kV) by mounting the as-prepared coating on conducting carbon tape and sputter coating with Pt to improve conductivity.

4.7 Results and Discussion

The phosphate ion undergoes speciation at different pH values to yield H₂PO₄⁻, HPO₄²⁻, PO₄³⁻ species.¹⁷ Ca²⁺ forms insoluble phases with all phosphate species, whereby it is not possible to stabilize a bath containing Ca²⁺ and phosphate, unless the [Ca²⁺] concentration is very low, below what is indicated by the solubility products of different
calcium phosphate phases. A bath with such low concentrations would not have adequate Ca\textsuperscript{2+} ions to coat a macroscopic object. One way of generating a high Ca\textsuperscript{2+} bath with a low concentration of free Ca\textsuperscript{2+} ions, is to add a complexing agent such as EDTA.

\[
\text{Ca}^{2+} + \text{EDTA}_2^{2-} \leftrightarrow \text{CaEDTAH}_2
\]

The Ca-EDTA complex has a high stability constant, whereby the free [Ca\textsuperscript{2+}] concentration is driven below the solubility product. On pH changes at the electrode the complex undergoes hydrolysis (base hydrolysis at cathode and acid hydrolysis at anode) to release Ca\textsuperscript{2+} ions. As the Ca\textsuperscript{2+} ions are deposited in the phosphate coating, they are replenished by the dissociation of the complex, thereby assisting prolonged electrodeposition. The rate of release of Ca\textsuperscript{2+} can also be controlled by varying the ligand. Complexes with a low stability constant yield conditions of higher degree of supersaturation in the bath. To this end we compare lactic acid with EDTA.

Within a few minutes of electrolysis of a Ca-EDTA bath, a white coating appears on the cathode. The presence of phosphate ions in the deposit could be easily verified in the IR spectrum of the coating. Fig. 4.8 shows the IR spectrum of the as-deposited coating. A broad absorption around 3500 cm\textsuperscript{-1} corresponds to OH stretching and peaks around 500 cm\textsuperscript{-1} correspond to P-O bending and peaks around 1000 cm\textsuperscript{-1} correspond to P-O stretching of PO\textsubscript{4}\textsuperscript{3-}.\textsuperscript{18} Observed peaks match with the vibrational frequencies of hydroxyapatite and this confirms that the as-deposited coating is a hydroxyapatite phase.

XRD patterns of the coatings obtained from a bath containing 0.05 M Ca(NO\textsubscript{3})\textsubscript{2} and 0.025 M EDTA ([Ca\textsuperscript{2+}]/[EDTA] = 0.5) at different deposition temperatures are shown in Fig. 4.9. The XRD pattern (Fig. 4.9a) of the coating obtained at 65°C shows most of the reflections corresponding to hexagonal hydroxyapatite phase. As the deposition temperature is increased (75-85°C), the XRD pattern (Fig. 4.9b, c) shows a progressive enhancement in the intensity of the 002 reflection relative to other reflections. At 85°C, only one prominent peak corresponding to the 002 plane is observed. This kind of anomalous enhancement in the intensity of a select reflection is indicative of oriented crystallization.
Fig. 4.8 IR spectrum of a hydroxyapatite coating.

At a low temperature (65°C), stability of the metal ligand complex is high and free Ca\(^{2+}\) concentration is low, slowing down the rate of deposition. A slow rate of deposition leads to the growth of thermodynamically stable state with isometric growth. In HA, the stable state corresponds to an unoriented coating. As the temperature increases stability of the complex decreases and the rate of deposition increases and this leads to deposition of an oriented coating.

In order to check the effect of duration of deposition on orientation, deposition has been done at two different times (10 and 30 min). The XRD patterns (Fig. 4.10) of both the coatings show prominent peaks corresponding to the 002 plane but the overall intensity of the coating obtained at higher deposition time (30 min.) is greatly enhanced. There is no loss of orientation in the thick coating suggesting that orientation is not substrate directed, but solution mediated.
Fig. 4.9 XRD patterns of hydroxyapatite coatings obtained from a bath containing 0.05 M Ca(NO₃)₂ and 0.025 M EDTA at different deposition temperatures (a) 60 °C (b) 70 °C (c) 80 °C. Features marked by the asterisk are due to the stainless steel substrate.

In order to study the effect of bath concentration on orientation, electrodeposition was done from a bath containing 0.1 M Ca(NO₃)₂ and 0.05 M EDTA as the same [Ca²⁺]/[EDTA] ratio at two different temperatures. The XRD patterns (Fig. 4.11) of the coatings obtained at higher metal ion concentration shows all the reflections corresponding to hydroxyapatite and the degree of orientation is greatly reduced compared to the dilute bath.
Fig. 4.10 XRD patterns of hydroxyapatite coatings obtained at 80°C with different deposition times (a) 10 min. and (b) 30 min. Features marked by the asterisk are due to the stainless steel substrate.
Fig. 4.11 XRD patterns of hydroxyapatite coatings obtained from a bath containing 0.1 M Ca(NO₃)₂ and 0.05 M EDTA at different temperatures (a) 75°C and (b) 85°C. Features marked by the asterisk are due to the stainless steel substrate.
Fig. 4.12 shows the XRD pattern of the coatings obtained from a bath containing 0.05 M Ca(NO₃)₂ and EDTA ([Ca²⁺]/[EDTA] =1). In this case the XRD pattern of the coating obtained at 85°C deposition temperature shows a prominent reflection corresponding to 002 plane of hydroxyapatite.

Fig. 4.12 XRD patterns of hydroxyapatite coating obtained from a bath containing 0.05 M Ca(NO₃)₂ and 0.05 M EDTA at (a) 75°C and (b) 85°C deposition temperature. Features marked by the asterisk are due to the stainless steel substrate.
In order to study the effect of complexing agent on oriented crystallization of hydroxyapatite, electrodeposition has been done from a bath containing lactic acid. The XRD patterns of these coatings are shown in Fig. 4.13. The coating obtained at 65°C deposition temperature shows prominent peak corresponding to 002 plane.

The stability of the Ca-Lactate complex is less than that of the Ca-EDTA complex. Because of the lower stability, the free Ca\textsuperscript{2+} released is large and the rate of deposition is fast. This leads to the deposition of oriented coating at 65°C itself.

![XRD patterns](image)

**Fig. 4.13** XRD patterns of hydroxyapatite coating obtained from a bath containing 0.05 M Ca(NO\textsubscript{3})\textsubscript{2} and lactic acid at different deposition temperatures (a) 65°C (b) 75°C and (c) 85°C. Features marked by the asterisk are due to the stainless steel substrate.
Typical SEM images of the unoriented and 002 oriented hydroxyapatite coatings are shown in Fig. 4.14. The unoriented coating has rounded crystallites and the 002 oriented coating has a flat surface. Evidence for secondary nucleation can be seen in the form a few spherical crystallites growing out of the base coating. The base coating is responsible for the observed 002 orientation of the hydroxyapatite coatings. When the secondary crystal growth increases, unoriented coatings are obtained.

![SEM images](a) ![SEM images](b)

**Fig. 4.14** SEM images of the unoriented (a) and 002 oriented (b) Hydroxyapatite coatings.
4.8 Conclusion

Unoriented and 002 oriented hydroxyapatite coatings have been deposited on stainless steel substrates. With EDTA as complexing agent, the 002 orientation increases with increase in deposition temperature due to the weakening of the stability of the complex. When a weak complexing agent such as lactic acid is used, the coatings show 002 orientation even at low deposition temperature and the extent of orientation increases with increase in deposition temperature. The extent of orientation also depends on the concentration of Ca$^{2+}$ in the bath.
References


