

Electrochemical and electrophoretic deposition of hydroxyapatite for orthopaedic applications

N. Eliaz¹, T. M. Sridhar^{*2}, U. Kamachi Mudali³ and Baldev Raj³

The basic calcium phosphate mineral, hydroxyapatite (HAP) ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), is the prototype of one of the major constituents of bone and teeth. Thin layers of HAP were coated on the surface of type 316L stainless steel by electrophoretic deposition (EPD) from a 2.5% suspension in isopropyl alcohol, and this was followed by vacuum sintering at 800°C for 1 h. The development of HAP coatings was affected by applied potential and time. In addition, HAP coatings were synthesised on pure Ti by electrochemical deposition and fully characterised to validate their use in orthopaedic implants. Electrodeposition was carried out from a bath containing low concentrations of $\text{Ca}(\text{NO}_3)_2$ and $\text{NH}_4\text{H}_2\text{PO}_4$ at pH 6.0 by cathodic polarisation. Both types of HAP coating were fully characterised, including with respect to corrosion resistance. The advantages of these techniques include: (i) control over the composition and structure of the coating; and (ii) the ability to coat irregular surfaces easily.

Keywords: Corrosion, Electrochemical deposition, Electrophoretic deposition, Hydroxyapatite coatings, Phase parity, Surface morphology

Introduction

Metals and alloys have a large range of applications, including devices for fracture fixation, partial and total joint replacement, external splints, braces and traction apparatus, as well as dental amalgams. Although they typically exhibit high strength and toughness, they are susceptible to chemical and electrochemical degradation. Such implant materials may corrode/wear, leading to the generation of particulate debris, which may, in turn, elicit both local and systemic biological responses.¹

Type 316L stainless steel (316L SS) is a widely used material for implant fabrication in orthopaedic applications. It possesses good inherent mechanical properties, reasonable corrosion resistance, biocompatibility, high tensile strength and suitable density for load bearing purposes. Ti and its alloys have found increasing use in the past two decades, owing to their low density, excellent corrosion resistance and biocompatibility. Ti develops a tenacious stable oxide film in aqueous solutions, mainly consisting of TiO_2 , which is responsible for the excellent corrosion resistance of the material. However, failures due to corrosion of stainless

steels and wear of Ti and its alloys do occur, generating greater amounts of metallic particles and loose implants. Among various modifications, coating technologies have emerged as a viable process and have opened up new opportunities for implants and prosthetic devices. Calcium phosphate coated on metal implants provides the necessary porosity for bone ingrowths, while the underlying metal substrate bears the load, the full weight bearing capacity being ensured soon after surgery. The major requirement related to the development of hydroxyapatite (HAP) coatings on metallic implants is preparation of a stoichiometric powder material (i.e. Ca/P ratio around 1.67) with preferred chemical and phase properties, close affinity with the bone tissue, and ease of deposition on irregular shapes.

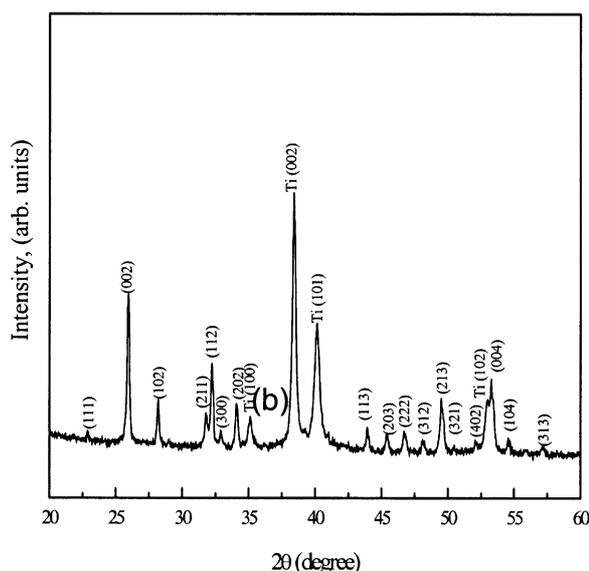
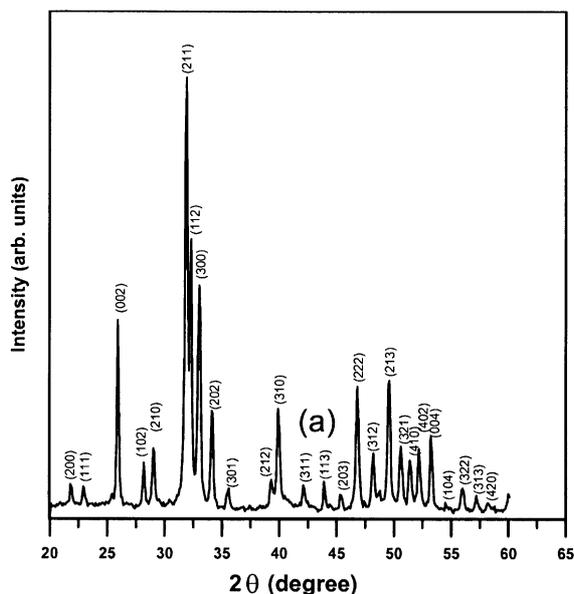
Electrophoretic deposition (EPD) of HAP on metal substrates has been studied in an attempt to achieve uniform distribution of fine HAP deposits. The advantages of this technique are high purity of layers formed, ease of obtaining the desired thickness, and strong layer adhesion to the substrate. The bond strength of the coatings is achieved by sintering; thus, shrinkage and cracking of the coating might occur during this process. Electrochemical deposition (ECD) is a potentially attractive process for synthesising bioceramic coatings from aqueous solutions on metallic implant surfaces.² Ease of process control, a wide range of coating compositions and suitability for complex implant geometries are characteristics that have made ECD methods increasingly popular. Hence, the various parameters affecting the formation of the HAP coatings by EPD and ECD techniques and their properties were evaluated in this work.

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1 XRD patterns of *a* HAP coated 316L SS (EPD, 60 V, 3 min, after sintering in vacuum at 800°C) and *b* HAP coated CP-Ti (ECD, -1.4 V v. SCE, 3 h, 90°C)

Experimental procedure

Electrophoretic deposition of HAP on type 316L stainless steel

HAP powder was electrophoretically deposited on the surface of 316L SS alloy (exposed surface area $\sim 1 \text{ cm}^2$) from a 2.5% suspension in isopropanol. The electrophoretic yield on 316L SS substrate was determined at a constant voltage of 60 V for various time intervals (2–5 min). The coatings were sintered at 800°C for 1 h in a vacuum furnace at 10^{-5} torr. Potentiodynamic polarisation studies of the uncoated and HAP coated samples were carried out in simulated body fluid (Ringer's solution (9 g L⁻¹ NaCl, 0.42 g L⁻¹ KCl, 0.2 g L⁻¹ NaHCO₃, 0.24 g L⁻¹ CaCl₂) at pH 7.4 and a temperature of $37 \pm 1^\circ\text{C}$). The critical parameters, such as corrosion potential (E_{corr}), breakdown potential (E_b) and repassivation potential (E_p), were evaluated from the polarisation curves. The details of the experimental parameters are reported elsewhere.^{3,4}

Electrochemical deposition of HAP on pure Ti

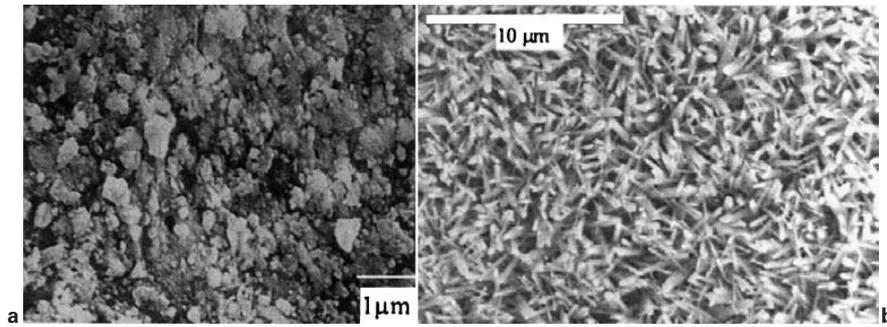
HAP was electrochemically deposited on commercially pure Ti Grade 2 sheet ($\sim 1 \text{ cm}^2$) by dissolving 0.61 mM Ca(NO₃)₂ and 0.36 mM NH₄H₂PO₄ in Millipore water, while adjusting the pH to 6.0. An EG&G/PAR 263A potentiostat/galvanostat, operating in potentiostatic mode, was employed to maintain a potential of -1.4 V v. SCE for 3 h at 90°C. The structure of the deposits was analysed by X-ray diffraction (XRD; Scintag diffractometer), and the morphology was analysed by scanning electron microscopy (SEM; Jeol model JSM-6300). Attached energy dispersive spectroscopy (EDS; Oxford Isis system) was used to estimate the Ca/P ratio in the deposits. Electrochemical measurements (EG&G/PAR 263A) of the uncoated and coated samples were carried out in Ringer's solution. The specimen was scanned in the positive direction at a sweep rate of 1 mV s^{-1} , and then in the negative direction after reaching a potential of 4.5 V; during this time the current was monitored with respect to the potential.

Results and discussion

XRD and SEM analyses

The degree of crystallinity influences the dissolution and biological behaviour of HAP coatings. Earlier studies have shown that a highly crystalline structure yields less dissolution of the coating.⁵ An XRD pattern obtained for a 316L SS sample electrophoretically coated at 60 V for 3 min and vacuum sintered at 800°C is shown in Fig. 1a. Another pattern, for CP-Ti coated through ECD, is shown in Fig. 1b. These two patterns look similar with respect to the crystallographic structure of the coating. The XRD patterns show diffraction peaks with minimal line broadening and high intensities, resembling the highly crystalline, stoichiometric HAP. No other calcium phosphate phases are observed. The strongest lines in these XRD patterns correspond to reflections from the (002), (211), (112), (300), (202), (222) and (213) planes of HAP, when indexed with respect to JCPDS file #09-0432. In addition, preferential crystal orientation of HAP at the [002] direction is indicated by a sharp peak at $\sim 26^\circ$, as previously reported by others for HAP coatings.⁶ As mentioned above, other crystalline phases, e.g. tricalcium phosphate, are not detected.

The surface morphologies of the coated samples obtained by EPD and ECD are illustrated in Fig. 2. Figure 2a shows a fairly uniform distribution of particles, indicating that the coatings are dense and microporous. No cracking of the coating is observed, suggesting that there was no significant shrinkage of the coating. This result confirms that the electrophoretic processing approach is very convenient in terms of obtaining dense samples after sintering. The surface morphology of the Ti electrodes after ECD with HAP is shown in Fig. 2b. This coating consists of a network of uniformly arranged large granules, each composed of finer equiaxed nanometric crystals (evident by atomic force microscopy), uniform and free of cracks. These results support the previous XRD data, indicating the formation of only the stoichiometric HAP phase. Moreover, EDS data of the ECD HAP are in fairly



2 SEM micrographs of *a* HAP coated 316L SS (EPD, 60 V, 3 min, after sintering in vacuum at 800°C) and *b* HAP coated CP-Ti (ECD, -1.4 V v. SCE, 3 h, 90°C)

good agreement with the FDA guidance for a Ca/P ratio between 1.67 and 1.76 and maximum 50 ppm heavy metals in the coating.⁷

Open circuit potential–time measurements

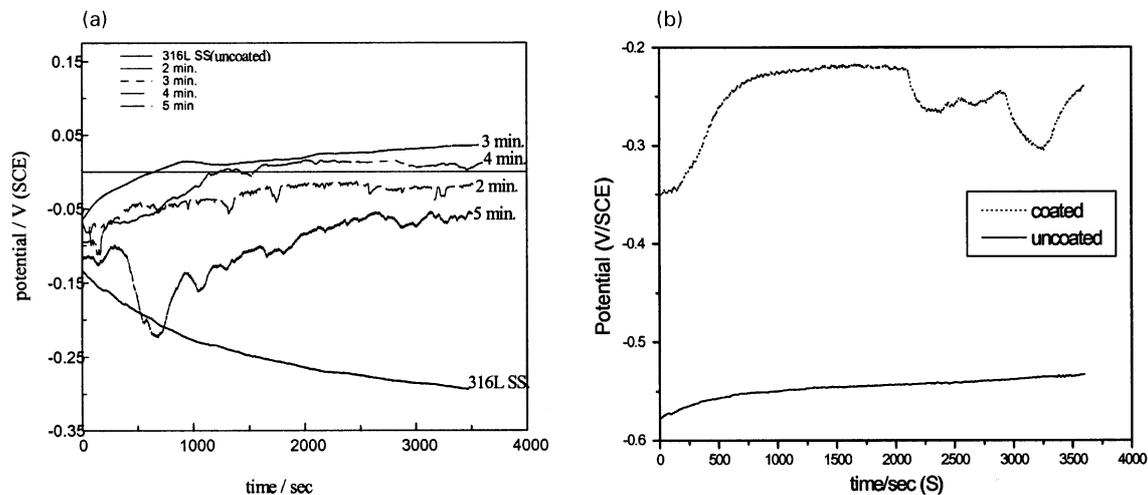
The open circuit potential (OCP)–time plots for uncoated and HAP coated 316L SS (EPD, 60 V, various deposition times) are shown in Fig. 3*a*. The OCP of the uncoated sample shows a decline in the active direction, until a steady state potential is almost attained. In contrast, the OCP of all HAP coated samples increases with time towards a nobler potential, and a steady state is typically reached within a short span of time, indicating that the coatings remained intact. The time required to attain steady state was considerably shorter for a sample coated for 3 min than for samples coated for either 4 or 5 min.⁴ This could be due to an increase in the weight of the coating and its porous nature. The noble behaviour of the sample coated at 60 V for 3 min may be attributed to the stable behaviour of the coated surface.

In the case of CP-Ti deposited by ECD, the OCP was found to be shifted considerably more in the noble direction compared to the uncoated sample (Fig. 3*b*). This shift of OCP and its saturation as a stable potential indicates the formation of a stable HAP/Ti interface. OCP values of -577 mV and -238 mV were obtained for the uncoated and HAP coated CP-Ti, respectively. This large difference indicates that the ECD coating has a protective nature. It can be seen that there are more

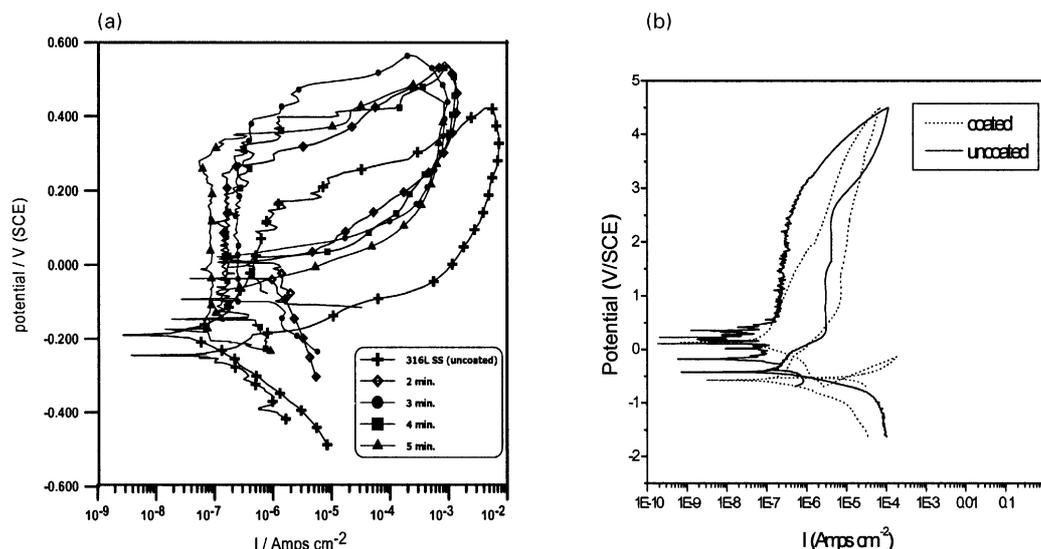
positive values of potential for the stainless steel substrate coated by EPD as compared to the Ti substrate coated by ECD. It should be noted that comparison of the absolute values is invalid, as not only are the substrate and deposition process different, but these two plots were obtained by two different laboratories that followed slightly different protocols.

Cyclic polarisation studies

The cyclic polarisation curves for uncoated and HAP coated 316L SS samples in Ringer's solution are shown in Fig. 4*a*. For the uncoated stainless steel, E_b and E_p values of +0.323 V and -0.221 V, respectively, were recorded with a large hysteresis loop. The area of the hysteresis loop is a direct measure of the pit propagation kinetics.⁸ The hysteresis loop with a considerable area observed for the uncoated steel indicates the extensive operation of a pit propagation mechanism. At the onset of film breakdown, there is a tremendous increase in the corrosion current density; that is, a larger hysteresis loop is observed. E_b and E_p for a sample coated at 60 V for 3 min are +0.508 V and +0.033 V, respectively.³ However, the breakdown potentials of samples coated for 2, 4 and 5 min are +0.465, +0.491 and +0.435 V, respectively. This means that the optimal time for HAP coating through EPD is 3 min. The breakdown potentials of all coated samples were found to be nobler than that of the uncoated steel, indicating improved corrosion resistance of the coated samples.



3 Open circuit potential in Ringer's solution v. time plots for *a* uncoated and HAP coated 316L SS (EPD, 60 V, different deposition periods) and *b* uncoated and HAP coated CP-Ti (ECD)



4 Cyclic polarisation curves in Ringer's solution for *a* uncoated and HAP coated 316L SS (EPD, 60 V, different deposition periods) and *b* uncoated and HAP coated CP-Ti (ECD)

Figure 4b shows the cyclic polarisation curves obtained for uncoated and HAP coated CP-Ti. The passivation current density of the uncoated sample was marginally lower than that of the coated samples. At 1.5 V, within the passive region, current densities of $3.47 \times 10^{-6} \text{ A cm}^{-2}$ and $8.02 \times 10^{-6} \text{ A cm}^{-2}$ were recorded for the uncoated and coated samples, respectively. The smaller size of the loops obtained for coated samples indicates the stability of the HAP/Ti interface against corrosion attack and the faster repassivation tendency of the HAP coatings.

In summary, stoichiometric HAP coatings can be obtained by EPD and ECD processes. In the case of EPD of HAP on 316L SS, applied potential and time affect the development of HAP coatings. The coating weight and thickness were both found to increase with the increase in applied potential and period of deposition.⁹ The increase in coating weight of the HAP coating is not necessarily desirable, because delamination of the coating from the substrate becomes more pronounced. The properties of the coatings remained unaffected upon vacuum sintering, for which the optimum conditions were found to be 800°C for 1 h at 10^{-5} torr. *In vitro* electrochemical studies show a shift in the OCP and pitting potential parameters in the noble direction for the HAP coated samples when compared to uncoated 316L SS.

For ECD of HAP on pure Ti, the pH of the solution, applied cathodic potential and bath temperature influence the nature of the coatings obtained. The process for electrodepositing HAP has been reported by Redpenning *et al.* to involve two steps, the nucleation of a calcium phosphate apatite mineral at the metal surface and the development of the mineral layer through constant composition precipitation.¹⁰ During this process, electrolysis of water leads to a local increase in pH at the cathode surface (due to the formation of OH^- and H_2). When occurring in a stable calcium phosphate solution supersaturated with apatite, this pH rise increases the PO_4^{3-} concentration, thus inducing even higher supersaturation of calcium phosphate salt and leading to homogeneous precipitation. The calcium phosphate is probably not nucleated on the metal surface. Instead, the precipitation may take place in solution, and the mineral particles reach the metal

surface by gravity and electrophoretic attraction. Such a process will result in a fairly constant average size of spherules over time, as observed in this work. However, because the bulk solution remained clear during deposition, the precipitation of calcium phosphate far from the metal surface can be excluded. A better understanding of the electrochemical reactions taking place at different pH and potential values is required to further improve the quality of the HAP coatings and the kinetics of their formation.

The results indicate that HAP coatings obtained by EPD and ECD should be considered as a viable alternative for improving the corrosion resistance and biocompatibility of the implant devices.

Conclusions

1. Type 316L SS was successfully coated with bioactive HAP using EPD, while pure Ti was coated by ECD.
2. XRD analysis confirmed the phase purity and stoichiometric characteristics of HAP coatings, and a uniform distribution of deposits was observed by SEM.
3. The electrochemical studies in Ringer's solution revealed that HAP coated samples exhibit higher corrosion resistance than uncoated 316L SS, with nobler OCP values, and higher breakdown and protection potentials. The uncoated 316L SS was found to be highly susceptible to corrosion attack. The smaller size of the loops obtained with HAP coated CP-Ti indicates the stability of the HAP/Ti interface against corrosion attack and the faster repassivation tendency of the HAP coatings.
4. The above results conclude that both coating processes may be used to modify the surface of the currently used 316L SS and pure Ti orthopaedic implant devices. They can provide a bioactive stoichiometric HAP top layer with good electrochemical and biochemical stability in the human body environment.

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