



# A comparative study on surface morphology and electrochemical behaviour of hydroxyapatite-calcium hydrogen phosphate composite coating synthesized in-situ through electro chemical process under various deposition conditions

Rajib Chakraborty\*, Partha Saha

Department of Mechanical Engineering, Indian Institute of Technology Kharagpur, 721302, India

## ARTICLE INFO

### Keywords:

Electro chemical deposition  
Hydroxyapatite coating  
Electro impedance spectroscopy  
Corrosion behaviour in SBF

## ABSTRACT

Coating surface energy and morphology play an essential role to decide on cell attachment and subsequent faster-uniform-interconnected cell growth over the coated orthopaedic metallic implant surfaces. It has been observed that during the process of electro-chemical deposition, the in-situ formed bond energy and deposited morphology greatly depend on few controllable process parameters namely reaction over potential, pulsed time and cathode current density. Keeping in view of this, this work aimed to study and compare the surface morphology and electrochemical corrosion resistance behaviour with respect to various depositions kinetics and nucleation mechanism achieved with the help of variable current density, voltage and time.

SEM micrographs of the electrodeposited surfaces depict the formations of altogether different structures of coating surfaces, varying from surface parallel flakes to concentric bars along with sub-micron dots and nano pores on its surfaces. It is observed that with increasing nucleation rate vis-à-vis increasing deposition potential, the presence of calcium orthophosphate phase is decreased along with increased rate of hydroxyapatite phase in the coating. The presence of various phosphate bond structures is evident from IR spectroscopy, which seems to be accountable for the formation of various morphologies along with the varying structure of hydroxyapatite. The electrochemical impedance spectroscopy study under contact with simulated body fluid (SBF) compared their performance regarding corrosion resistance capability of coating surface after implantation in the human body.

## 1. Introduction

Metallic implants made out of stainless steel and titanium alloy are widely used as on date for most load-bearing implants in the human body on account of their high corrosion resistance and superior mechanical stability and performance [1–3]. However, these metallic alloys show a major shortcoming that they are unable to form strong and uniform bonding with surrounding tissues or bones on account of surface energy variation on metallic surfaces in the presence of various grain structures with varying crystal planes parallel to contact surface [4–6]. Also, it is observed that in few cases the non-uniform growth of tissues over the metallic implant surfaces due to the local variation of alloying elements leads to a major cause for the failure of implants on account of poor bonding and toxicity. Continuous research development is in place to develop biocompatible and corrosion resistant thin coating over those metallic implants surfaces in view of uniform

bonding of surround tissues along with faster cell growth [7–9]. In this regard, ceramic coatings, consisting of calcium phosphate and its group compounds, seem to be the most effective from both biocompatibility and corrosion resistance point of view. It is also observed that human bones consist of similar kind of different calcium phosphate compounds along with the presence of few other minerals and materials [10,11].

Over the last decade, several techniques were tried to develop a coating of bio-active hydroxyapatite and calcium phosphate over the implant material [12,13]. A few successful coating techniques are sol-gel technique, pulsed laser deposition, laser cladding etc. [14]. Among these methods, only plasma spray method is clinically accepted till now. However, plasma spray method suffers from some drawbacks, such as extremely high application temperature, which affects the homogeneity of the coatings and structure of metallic implants, because of unpredictable phase changes of calcium-phosphorous ceramic during coating, particle release and delamination [15]. On the other hand, the

\* Corresponding author.

E-mail address: [rajibju4@gmail.com](mailto:rajibju4@gmail.com) (R. Chakraborty).

electro-deposition method, which is becoming popular as on date, has added advantages of formation of nano-crystalline material coating over implant surface due to in-situ reactions between ions over the surface along with a uniform distribution of coating layers throughout the implant surfaces without getting interacted with notch and complex structure of implants.

Thanh et al. showed how the in-situ formed hydroxyapatite structure, morphology and composition of the coating affected with varying electrolyte concentration, temperature and precursor concentration during electro-deposition process [16].

Najasi et al. showed that morphology along with chemical bond of the hydroxyapatite coating formed through pulsed electro-deposition process varied with deposition current density vis-à-vis in-situ nucleation rate, and thus the same also affected the biocompatibility of the overall coating [17].

The present authors showed, in their previous studies, how coating morphology, the degree of crystallinity and amount of hydroxyapatite phase present in the coating were varied with varying rate of in-situ nucleation vis-à-vis cathode current density. It was also evident that degrees of crystallinity and the relative amount of hydroxyapatite phase present in the coating had a significant influence on cell cytocompatibility and growth factor over the coating surfaces [18–20].

Keeping in view of this, this study aims to compare and establish the relationship between formed surface morphology along with the electrochemical behaviour of the coating surfaces with respect to different nucleation mechanisms and growth rates of the in-situ formation. On one side the nucleation growth rate is controlled with varying cathode current density, and on other side, the reaction mechanism vis-à-vis structure is controlled with the help of varying over-potential during depositions.

## 2. Materials and methods

### 2.1. Materials

Commercial grade stainless steel (SS316) sheet of 180  $\mu\text{m}$  thickness was used as substrates for electro-deposition. The substrate surface was polished with SiC emery papers (600 and 800 grit) followed by ultrasonic cleansing in distilled water and acetone for several times. Epoxy resin was used to mask the surface so that it leaves an exact exposed area on one side of the substrate for deposition.

### 2.2. Depositions of coatings

A typical two electrode system was used for the deposition. SS316 substrate with an exposed area of 5  $\text{cm}^2$  was used as the working electrode, and another SS316 substrate plate with an exposed area of 10  $\text{cm}^2$  was used as the counter electrode. The electrolyte solution was prepared by mixing 0.15 M of  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  (Merck, > 98% purity) along with 0.1 M of  $\text{NH}_4\text{H}_2\text{PO}_4$  (Merck, > 98% purity) salt in distilled water. The electro-deposition was carried out using Biologic SP150 electro-deposition set up in continuous, pulsed and pulsed reverse mode with constant cathode current density (5  $\text{mA}/\text{cm}^2$  and 10  $\text{mA}/\text{cm}^2$ ) and constant voltage (1 V, 2 V and 3 V).

### 2.3. Material characterization of coatings

The phase purity and crystallinity of the coatings were analysed by X-ray diffraction (Pan Analytical diffractometer), using  $\text{CuK}\alpha$  radiation (wavelength = 0.1564 nm), at a step angle of  $0.02^\circ$ , scanning rate  $0.05^\circ$  per second and two theta range between 10 and  $50^\circ$ . The percentage amount of different phases present in the coating was estimated with the help of Rietveld analysis using TOPAS 4.5 software of BRUKER, Germany.

The microstructure, compositions and surface morphology of the coatings were characterized by secondary electron images of SEM (EVO

18, Zeiss) combined with EDX (EDAX, USA). Further, in order to confirm the presence of phosphate group in the coating material, which is one of the major constituent of the complex chemical structure of hydroxyapatite, Fourier transform infrared spectroscopy (FTIR) was carried out in Nicolet 6700 spectrometer using KBr pallet technique in the range of 4000 to  $400\text{ cm}^{-1}$ , with a resolution of  $8\text{ cm}^{-1}$ . All measurements were performed at room temperature which was around  $25^\circ\text{C}$ .

### 2.4. Electrochemical behaviour assessment of coatings

The electrochemical behaviour under immersion in SBF was evaluated through electrochemical impedance spectroscopy (EIS) with the help of Biologic SP 150 device set up. A three electrode system, consisting of Ag/AgCl electrode as a reference electrode, platinized platinum as a counter electrode and coated sample as working electrode was used. EIS measurement was performed at OCP condition with a surface area of around 1  $\text{cm}^2$  for the working electrode at a frequency range of  $10^6$  to  $10^{-2}$  Hz with 10 mV amplitude. The impedance spectra were analysed with the help of biologic EC Lab software, and the results were reported in the form of standard Nyquist and Bode plots. An equivalent circuit was chosen for this analysis based on the review of similar research work in recent past on this type of biocompatible coating [21]. The SBF solution has the compositions, NaCl – 7.996 g/L, KCl – 0.224 g/L,  $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$  – 0.278 g/L,  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  – 0.305 g/L,  $\text{NaHCO}_3$  – 0.350 g/L,  $\text{K}_2\text{HPO}_4 \cdot 3\text{H}_2\text{O}$  – 0.228 g/L,  $\text{Na}_2\text{SO}_4$  – 0.071 g/L, which were recommended in various literature for examining the corrosion behavior of the implant materials.

Corrosion behaviour of deposited coatings in SBF solution was evaluated based on potentiodynamic polarization measurements, by using a potentiostat/galvanostat (Bio Logic SP150) with a standard three electrode cell. All potentials were referred to the saturated Ag/AgCl electrode (RE), in which SS316 strip was used as the counter electrode. The potentiodynamic polarization curve was obtained by scanning from  $-1.0\text{ V}$  to  $+1.0\text{ V}$  at a scanning rate of 1 mV/s. The corrosion current and voltage were calculated from the software directly by fitting the Tafel curve method. Stabilization time of around 60 min in SBF was set for each sample.

## 3. Results and discussion

### 3.1. Phase analysis

The X-ray diffraction patterns of all the coatings [Fig. 1] are in good agreement with the standard data of calcium hydrogen phosphate (04-013-3344) and hydroxyapatite (00-064-0738 and 00-055-0592) of ICDD database. Clear peak related to  $\langle 020 \rangle$ ,  $\langle 121 \rangle$ ,  $\langle 040 \rangle$  and  $\langle 112 \rangle$  planes of calcium hydrogen phosphate along with  $\langle 211 \rangle$  and  $\langle 202 \rangle$  planes of hydroxyapatite are evident in the diffraction patterns. In the coatings formed at a lower voltage (1 V) and lower current density (5  $\text{mA}/\text{cm}^2$ ), texture effect is evident corresponding to  $\langle 020 \rangle$  plane of calcium hydrogen phosphate phase. With increasing voltage and current density vis-à-vis increasing reaction over-potential and nucleation rate, the  $\langle 020 \rangle$  plane formation of calcium hydrogen phosphate is restricted. The same can be witnessed with lower texturing co-efficient in the diffraction pattern. Thus it may be presumed that the second phase of in-situ reaction (conversion of calcium hydrogen phosphate into hydroxyapatite phase) is more favourable at higher nucleation rate.

Further, on the detailed comparison of diffraction patterns [Fig. 2], it is evident that with increasing reaction potential or cathode current density the nano-crystalline formation of calcium hydrogen phosphate phase is favourable on account of faster reaction kinematics. Whereas, the internal stress generation during crystal formation is much lower in case of pulsed electro-deposition as compared to continuous depositions under constant cathode current density of 10  $\text{mA}/\text{cm}^2$ . High intensity broad diffraction peaks of  $\langle 211 \rangle$  and  $\langle 202 \rangle$  planes of hydroxyapatite

Download English Version:

<https://daneshyari.com/en/article/7001129>

Download Persian Version:

<https://daneshyari.com/article/7001129>

[Daneshyari.com](https://daneshyari.com)