Paper No.
SS32

CORCON
17-20 September
Mumbai, India
2017

Bioresorbable nano β-TCP coatings on titanium by EPD for Biomedical Applications

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ABSTRACT

Biodegradable tricalcium phosphate [$Ca_3(PO_4)_2$, β-TCP (whitlockite)] coatings were developed on titanium by means of electrophoretic deposition (EPD) to improve the corrosion resistance and biocompatibility. As a bioresorbable biomaterial, on implantation it would naturally be absorbed by the body resulting in the formation of new bone tissues. Nano β-TCP powder was synthesized by wet chemical precipitation method and coated on titanium surfaces by EPD. The coatings were carried out at various potentials ranging from 10-50 V and were followed by sintering in vacuum at 800°C for 1h. The optimum coating parameters were obtained at 30 V and 3 minutes by EPD. The crystallinity, vibrational states, and surface morphology were characterized by XRD, FTIR and FESEM respectively.

The corrosion resistance of the coatings was further evaluated electrochemically to study the stability of the coatings using open circuit potential-time measurements (OCP), electrochemical impedance (EIS) and anodic polarization studies in Ringer's solution. The electrochemical studies indicate the stable nature of nano β-TCP coatings on the titanium substrate.

Keywords: nano β-TCP, EPD, Titanium, Electrochemical studies.

1. INTRODUCTION

The improved corrosion resistance, mechanical strength, biocompatibility and light weight of titanium and its alloys makes it a suitable candidate as an implant material in orthopedic and dental applications. These properties are superior to stainless steel and Co-Cr alloys [1-3]. The service life of metallic implant is affected by corrosion and wear resistance, tissue reactions, surface conditions, and osseointegration. Hence the need of surface modification of these materials is required and also to enhance their bioactivity and osseointegration capabilities[4]. β-tricalcium phosphate[$Ca_3(PO_4)_2$ which is commonly known as β-TCP] has Ca/P ratio of 1.5 [5]. β-TCP is a bioresorbable bioceramics,which gets resorbed and helps in the formation of new bone tissue, thereby replacing the implanted β- TCP [6]. It exists in two allotropic forms, α and β tricalcium phosphate. Generally β-TCP is formed at low temperature around 700°C and it is converted into α-TCP at 1125°C [7, 8]. Beyond this temperature, α- TCP phase is stable up to 1430 oC. Usually, the crystal forms of β-TCP are called as whitlockite [9]. A resorbable β-TCP is the best implant, which starts to degrade and helps in regeneration of bone tissues that leads to better interfacial stability [10]. But it shows higher solubility than hydroxyapatite (HAP) which is a bioactive ceramic. This leads to fast degradation inside the body and there will be a moderate resorption rate for the formation of new bone tissues [11]. Hence β-TCP is considered as the most fascinating material in biomedical applications. The low mechanical properties prevent us from using it directly as an implant material. Many techniques such as electrodeposition [12], metal organic chemical vapor deposition [13], Plasma spraying [14], Micro-arc oxidation [15], electrochemical [16] and electrophoretic deposition (EPD) [17] are available for the development of bioceramic coatings on titanium. Among these techniques EPD method was chosen to achieve a fine accumulation of the particles on the substrate from alcoholic suspension. EPD includes several advantages such as simple equipment, rate of deposition can be controlled by varying applied voltage, low cost and coating process can be completed in a few minutes [18].

The present work describes the synthesis of n-β-TCP by wet chemical precipitation method and to deposit it on titanium metal by EPD. The coated samples were sintered at 800°C for 1 h in a vacuum furnace (10^{-5} Torr). These coated samples were optimized by means of electrochemical studies in Ringer's solution.

1. EXPERIMENTAL PROCEDURE

2.1 Specimen and suspension preparation for EPD

Titanium electrodes of 10×10×3 mm size samples were mechanically polished using Silicon carbide papers from 120 to 1000 grit with polishing machine. The samples were degreased with acetone and ultrasonically cleaned using deionized water. Polished Ti was used as a cathode and 314 SS Sheet of 11×8×0.5 mm dimension were used as an anode. EPD of n-β-TCP on titanium metal was carried out at room temperature. A 100 ml beaker was taken with 1.5% suspension of nano powder and it was closed with teflon covering. The two electrodes were dipped in the suspension and the distance to be maintained between two specimens was 10 mm. Deposition was carried out on 1cm^2 surface area and the other edges and sides of titanium were masked with non-conducting Teflon tape. EPD was achieved with varying applied potentials 10 – 50 V and at constant time of 3 minutes. The coated samples were sintered at 800 ^{o} C in Vacuum for 1 h.

2.2 Electrochemical studies

The corrosion studies of both n-β-TCP coated and uncoated titanium were carried out using Ringer's solution (NaCl-8.60, CaCl2-0.33, KCl-0.30 and NaHCO3-0.2 g/l respectively). The functioning of the electrochemical measurements were done by a conventional three electrode system at 37 ^{o}C. Saturated calomel electrode (SCE) was used as reference electrode, graphite was used as auxiliary electrode and TCP coated titanium was used as working electrode respectively. The electrochemical measurements were carried out on both uncoated and TCP coated on titanium are open circuit potential (OCP)-time measurements, potentiodynamic polarization studies and electrochemical impedance studies. These studies were carried out using Biologic SP-240. A flat corrosion cell was used to measure the corrosion behavior of uncoated and TCP coated sample. The exposure of the sample in the solution was 1 cm^2.

3. RESULT AND DISCUSSION

3.1 EPD OF n-β-TCP ON TITANIUM

The changes in weight gain of nano β-TCP coatings on titanium at different voltages (10-50 V) and at a constant time of 3 minutes is given in Figure 1. The rate of deposition of suspended particles increases with increase in applied potential. The quality of deposits on the substrate were unaffected by the applied potential ranging from 10-50 V. The coatings did not develop any cracks but there was only a decrease in coating weight. This is due to rapid movement of the particles which leads to collision and non-uniformity. Uniform coatings can be obtained between 20 to 50 V and at time intervals from 1-5 minutes.

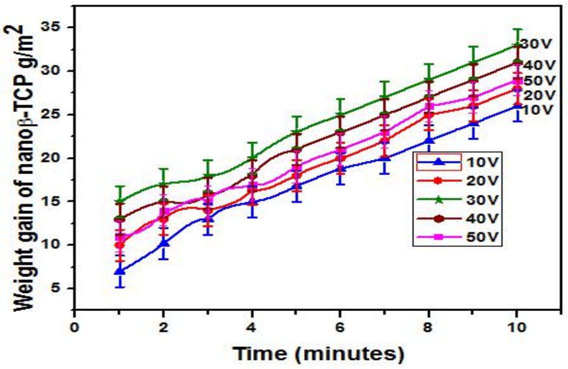

Figure 1: Changes in coating weight of nano β-TCP obtained with change in coating time (1- 10 minutes) at different voltages (10-50 V)

3.2 XRD

The coatings have the corresponding hkl indices of nano-TCP[19]. These values were indexed with JCPDS file number 090169, which confirms the presence of nano-TCP alone in the compound with sharp and intense peaks. The XRD patterns of both vacuum sintered and unsintered nano-TCP were found to be similar. Hence, there is no change in patterns after vacuum sintering. This shows the stable nature of nano-TCP coatings. The size of nano -TCP powder was calculated using Scherrer's equation are 47.87 nm, 48.26 nm and 50.29 nm respectively.

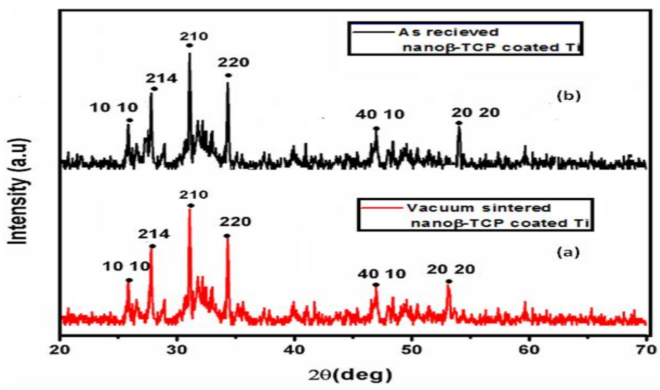

Figure 2: XRD patterns recorded for nano β-TCP coated Ti obtained at the optimum coating potential of 30 V and 3 minutes (a) vacuum sintering at 800 °C and (b) as received nano β-TCP coated Ti (before sintering)

3.3 FT-IR

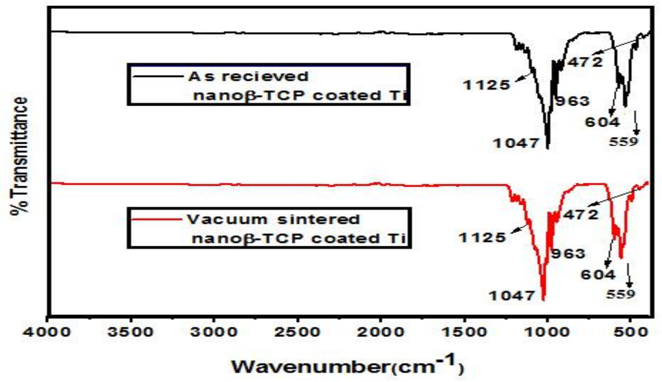

Figure 3: FT-IR of nanoβ-TCPcoated Ti obtained at the optimum coatingpotential of 30V and 3 minutes (a) vacuum sintering at 800°C (b) as received nano-TCP coated Ti (before sintering)

The spectra of nano-TCP powder coated on titanium at an optimum potential of 30 V and 3 minutes after sintering at 800°C in vacuum at 10^{-5} Torr for 1 hour in comparison with unsintered nano-TCP sample are shown in Figure 3 (a and b) respectively. The characteristic peaks of nano-TCP are present at 1125 and 1047 (ν_3), 559 and 604(ν_4) cm^{-1}corresponding to the phosphate bands. Hence, the bands at 900-1200 cm^{-1} correspond to the stretching mode of phosphate group and 559 and 604 cm^{-1} is vibrational mode of phosphate group [20]. The sintered and unsintered nano -TCP peaks were similar. This confirms the presence of nano-TCP as a single phase and is in agreement with the XRD patterns recorded. No new phases of calcium phosphates were detected.

3.4 FESEM

Figure 4(a) shows the formation of microporous layers of nano-TCPcoating on titanium for the unsintered sample as observed by FESEM. The particles on the substrate were uniform and no crack was observed on the surface. Figure 4 (b) shows the micrographs of vacuum sintered nano-TCPon titanium. The coatings were found to be denser and the particles were tightly packed after sintering. No cracks are observed after sintering.

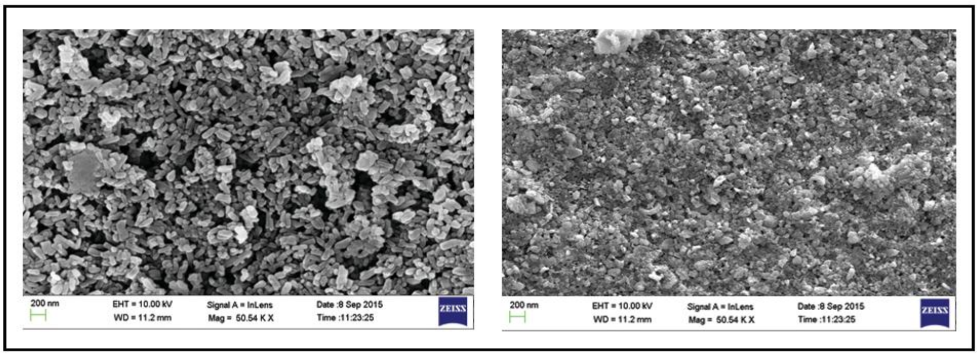

Figure 4: Surface morphologies of nano β-TCP coatings on Ti obtained at 3 minutes (a) before sintering and (b) after sintering in vacuum at 800°C.

3.5 Electrochemical studies

3.5.1 Open Circuit Potential-Time Measurements

The OCP-time plots for the uncoated titanium and nano β-TCP coated titanium at various potentials (10-50V) is shown in Figure 5. From the Figure we can observe that OCP of nano β-TCP deposited samples move towards positive direction and attains stable condition on comparison with the uncoated titanium metal. The potential of uncoated titanium sample shifts slightly towards the noble direction due to the presence of native passive layer on the metal surface. The maximum open circuit potential was reached after 60 minutes was at 30 V and 3 minutes compared to the uncoated samples.

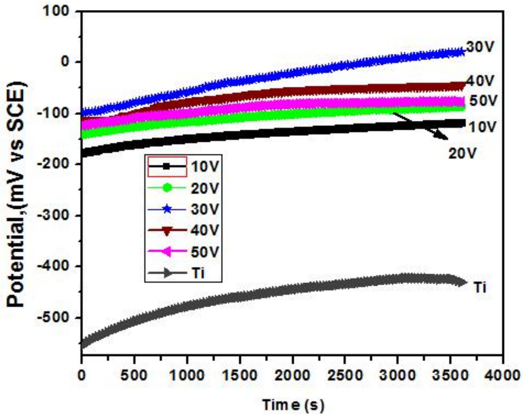

Figure:5 OCP – time measurements for uncoated and nano β-TCP coated Ti samplesobtained at different voltages (10-50V) at a constant time of 3 minutes in Ringer's solution

3.5.2 Electrochemical Impedance Spectroscopic Studies

Nyquist plots of both uncoated and coated samples are shown in Figure 6. Nanoβ-TCP coated titanium at 30V and 3 minutes shows maximum impedance when compared to uncoated titanium. The resistance and capacitance values of uncoated and coated samples are shown in Table 1. Equivalent circuit model of uncoated and coated sample is shown in inset of Figure 10. This equivalent circuit model is obtained after fitting the spectra of uncoated and nano-TCP deposited titanium metal by using (BioLogic – SP240) EC-Lab V10.37 software. The best fitting is chosen by considering small chi square values. When the chi square values are very small, it is considered as suitable spectra.

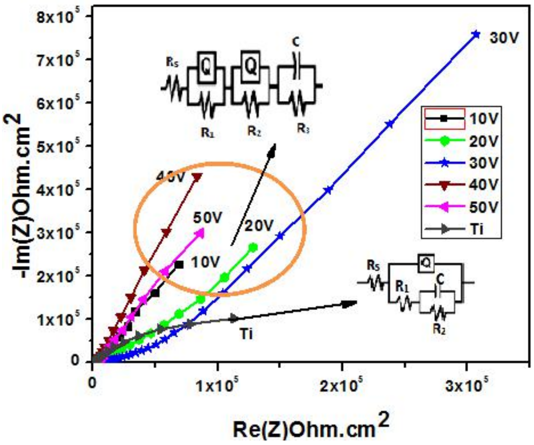

Figure 6: Nyquist Plots obtained for uncoated and nanoβ-TCP coated Ti at different voltages (10-50V) at a constant time of 3 minutes in Ringer's solution. Inset shows Equivalent circuit model of uncoated and nanoβ-TCP coated titanium

The equivalent circuit model for (a) nanoβ-TCP coated titaniumand (b) uncoated is shown in Figure 6. The equivalent circuit model for uncoated sample is [$R_s(R_1Q_1)(R_2C)$]. R_s represent solution resistance, R_1 and Q_1 represents polarization resistance and constant phase element of barrier oxide layer present on the titanium surface. R_2 and C indicate polarization resistance and double layer capacitance of metal surface. The EIS spectra model for nano β-TCP deposited titanium is shown in Figure 6 is [($R_s(R_1Q_1)(R2Q_2)(R_3C)$]. R_1 and Q_1 indicate polarization resistance and constant phase element of coated layer. R_2 and Q_2 indicate polarization resistance and constant phase element of passivation layer present in between metal surface and coated layer. R_3 and C represent polarization resistance and double layer capacitance of metal surface.

A constant phase element (CPE) is an imperfect capacitor which is introduced in the fitting for barrier and coated layer alone. This indicates that the coated layer controls the release of metal ions in to the solution and thus prevents the corrosion. The impedance of CPE can be expressed as expressed by the equation [21]. ------------------------------ (1)

where Q is the constant phase element(CPE), ω is the angular frequency and n is the exponent of CPE which is associated with non-uniform distribution of current and due to surface roughness with values between -1 and 1(0<n<1). If n is equal to one it behaves as an ideal capacitor. If n is equal to zero it describes a pure resistor.

Table 1: EIS spectra fitted values obtained for uncoated and nanoβ-TCP coated on Ti in Ringer's solution

Coating Potential	|Z|	R_S	Q_{Coat}	n_{Coat}	$R_{1(Coat)}$	Q_b	n_b	R_2	C_{dl}	R_3
Uncoated	100632	90.9	82.3×10^{-6}	0.88	224657	–	–	–	47.25×10^{-3}	15265
10V	238786	60	56.03×10^{-6}	0.77	44.82×10^{4}	60.47×10^{-6}	0.70	12.57×10^{3}	0.122×10^{-3}	20395
20V	296469	50	22.12×10^{-6}	0.73	4.18×10^{6}	26.21×10^{-6}	0.63	5.89×10^{5}	2.175×10^{-5}	24101
30V	818709	15.7	0.27×10^{-6}	0.62	2.014×10^{11}	0.139×10^{-6}	0.50	7.56×10^{8}	85.54×10^{-9}	78354
40V	438449	19.2	3.26×10^{-6}	0.66	3.58×10^{9}	10.67×10^{-6}	0.54	9.23×10^{7}	52.6×10^{-7}	52134
50V	311745	35.9	11.34×10^{-6}	0.71	5.235×10^{8}	21.5×10^{-6}	0.61	2.87×10^{6}	0.257×10^{-6}	9411

3.5.3 Potentiodynamic Anodic Polarisation Studies

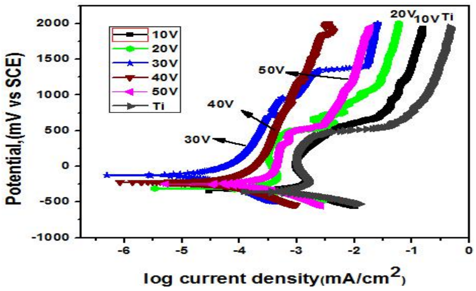

Figure 7: Potentiodynamic curves of uncoated and nanoβ-TCP coated Ti samples obtained at various coating potentials (10-50V) at a constant time of 3 minutes in Ringer's solution

Figure 7 shows the polarization curves of both uncoated and nano β-TCP coated titanium metal obtained at various coating potentials (10-50 V) at a constant time of 3 minutes in Ringer's solution. The E_{corr} and I_{corr} values of uncoated titanium sample were found to be -458.5V and 0.611μA/cm^2 and the optimized potential of 30 V was found to be -152.7 mV and 0.076 μA/cm^2. From these results we could analyze that nano-TCP coated titanium at 30 V and 3 minutes has more corrosion resistance than uncoated titanium.

5. Conclusions

The optimized potential for nanoβ-TCP coated titanium was obtained at 30 V and 3 minutes from a 1.5% suspension in ethanol by EPD. XRD, FTIR and RAMAN analysis confirmed the formation of nanoβ-TCP coatings on the metal surface. No other phases were detected. Electrochemical studies reveal more corrosion resistant behaviour for nanoβ-TCP coated sample when compared to uncoated sample. Cell attachment and cell proliferation is high in coated sample when compared to uncoated titanium. Bioceramic coatings have been successfully developed on Ti by EPD with enhanced corrosion resistance and biocompatibility for bone tissue engineering applications.

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