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A comparative study on the direct and pulsed current electrodeposition of hydroxyapatite coatings on surgical grade stainless steel

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ABSTRACT

Hydroxyapatite [$Ca_{10}(PO_4)_6(OH)_2$, (HAP)] coatings were developed on 316L stainless steel substrate from the electrolyte containing hydrogen peroxide (H_2O_2) with the concentration ranging from 600 to 3000 ppm by both the direct and pulsed current electrodeposition methods. The effects of direct current density upon the addition of H_2O_2 into the electrolyte on the phase purity and morphology of the as-deposited coatings were reported. The influence of pulsed parameters such as peak current density and pulse on and off time on the deposit compositions was also examined and compared with direct continuous current deposition in relation to the crystallinity, microstructure and the corresponding phases. X-ray diffraction (XRD) and Fourier transform infrared spectroscopic (FT-IR) techniques were performed in order to assure the purity, phase compositions of the coating and the morphology of the coating were characterized by scanning electron microscopic (SEM) technique. The results showed that the coating consists of mixed phases of calcium phosphate (Ca–P) in the absence of H_2O_2 in the electrolytic bath. Whereas the addition of H_2O_2 lowers the deposition current with the formation of smooth and uniform layer comprised solely of HAP. It is highly beneficial to increase the peroxide concentration from 600 to 2000 ppm for the deposition of pure HAP. While increasing the peroxide concentration to 3000 ppm, the coating morphology is not uniform as evidenced from the SEM result. Moreover, the increased adhesion and crystallinity of the HAP coating were achieved by pulsed current electrodeposition method at lower current density with longer pulse off time. The results of pulsed electrodeposition show that the relaxation time of the pulse is beneficial for the growth of HAP because it allows the diffusion of ions from bulk solution to the surface of electrode and thus lowers the concentration polarization in the next pulse on time. The combination of pulsed electrodeposition and addition of H_2O_2 into the electrolyte promisingly improve the physico-chemical properties of HAP coating.

1. Introduction

Metallic implants such as stainless steel (SS), titanium and its alloys and cobalt chromium alloys in the orthopedic prostheses have gained significant advantages in the recent years due to their immense mechanical features that satisfy the requirement of the human bone [1]. The need to reduce costs in public health services has compelled the use of austenitic stainless steel of the type 316L SS as the most economical alternative for orthopedic implants respecting to the other usual Ti or Co–Cr alloys [2]. It is traditionally used for implantation purposes like bone screw/plate, intra-medullary rod, fixation wire, HIP joint, and knee joint in orthopedic surgery owing to their general corrosion resistance, good mechanical properties and acceptable biocompatibility [3–5]. Moreover, in several countries it is customary to use 316L SS as temporary implants. The stainless steels protect themselves by forming passive oxide films on their surfaces which provide the key to their high resistance to corrosive attack. The low carbon content in the 316L SS provides an improved corrosion resistance in simulated physiological environments [6]. The presence of 2 to 4 wt.% Mo increases the resistance to pitting corrosion. Many surgeons, especially in developing countries, prefer stainless steels as implant materials based on millions of satisfactory clinical cases [7].

To further improve the biological performance and biocompatibility of 316L SS alloy, ceramic Ca–P coating is often applied to the surface to make the entire structure even more important. HAP has been recognized as being osteo-conductive, and is able to promote bone ingrowth and adhesion on the surface of the implant during the early stages of the implantation [8–10].

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Over the years, HAP coatings have been developed on metal surfaces by variety of methods including plasma spraying [11,12], sol–gel [13–15], electrophoretic deposition [16,17], biomimetic method [18] and ion beam deposition [19]. Though plasma spraying technique is the only clinically accepted method to deposit HAP, it has several limitations. For example, it is very difficult to control the composition and structure of the HAP coatings deposited, due to extremely high processing temperatures [20,21]. Secondly, this technique produces a non-homogenous coating which has poor adhesion due to the delamination of HAP from the substrate. Thirdly, this technique has a line-of-sight requirement, which greatly limits its usage in the coating being developed for implants [22,23].

In view of the various limitations of the plasma spray technique, research has been carried out on new methods of deposition. In recent years, electrochemical cathodic deposition (ECD) has some evident advantages such as the coating process at low temperature, controlled chemical composition, simple set-up and relatively low expense [24–27]. However, pure HAP coating developed by traditional electrochemical deposition has several major drawbacks which could limit the potential applications of this coating technique [28–31].

During ECD, an electric current is passed through the electrodes submerged in an electrolyte, initially the OH^- ions are produced at the substrate (cathode) due to the electrochemical reaction which is usually the reduction reaction of water, resulting in the formation of large amount of H_2 gas. H_2 gas adheres itself to the surface of the metal substrate, preventing further deposition of Ca–P, leading to a poor adherence of the coating to the substrate [32]. This electrochemical deposition often results in the deposition of monetite ($CaHPO_4$) or brushite ($CaHPO_4*2H_2O$) rather than HAP [28,29], and also pH generated at the substrate cathode, less favors the HAP formation. This problem can neither be solved by the application of higher current density, although this will lead to the generation of more OH^- ions at the surface resulting in the formation of more hydrogen bubbles. This phenomenon destroys the simple addition of base directly into the electrolyte as this will cause course precipitation in the bulk solution rather than deposition on the substrate. Moreover, in the electrodeposition process at cathode, upon the application of direct continuous current the loose, porous and low adhesive coatings can easily be developed. The prime reason may be due to the polarization of concentration differences which is produced because of the lower mobility of ions diffused from the main body of the solution to the surface of substrate.

To overcome these obstacles, several modifications are proposed to make on the direct current electrochemical deposition method more suitable in the following way. At the outset, H_2O_2 was added into the electrolyte during the deposition process and H_2O_2 can substitute for H_2O which in turn lowers the deposition current and change the mechanism of the whole lot of electrochemical reaction [33,34]. Due to this peroxide addition, the effects of H_2 evolution may be erased, and consequently, dense and uniform coatings may be formed [35]. Secondly, the pulsed current is applied to electrodeposit the HAP on 316L SS substrate which holds a relaxation time compared with direct continuous current. In the pulsed electrodeposition process, as current is applied, the ions closer to the cathode are adequately deposited. During the relaxation time, the diffusion of ions from bulk solution to the surface of cathode takes place, in such a way to improve the physico-chemical properties of coatings [34]. D.J. Blackwood et al. [33] reported galvanostatic pulse electrodeposition of HAP on titanium and demonstrated that periodic pulsed current densities gave a better adhesion of HAP coatings deposited on the substrate surface when compared to the continuous current density. However, the morphology of the coating deposited by pulsed current has not been investigated. Moreover, the pulsed parameters such as pulse off and on time and their effects on coating composition and morphology have not been studied so far. Yu et al. [34] used pulsed electrodeposition associated with H_2O_2 into the electrolyte to obtain HAP coatings with improved adhesion strength between the coating and substrate. However, they neither varied nor optimized H_2O_2 concentration and its effect on coating composition, morphology has not even been demonstrated. Very recently, another method has been proposed by Drevet et al. [36] who studied the effects of pulsed current and thereby H_2O_2 concentration on the phase composition, morphology of Ca–P coating deposited on Ti-6Al–4V. Even though H_2O_2 concentration was optimized, the morphology of the coating obtained from optimized conditions seems to be porous which is not much satisfactory. Moreover the current density and H_2O_2 concentration used in the deposition were high such as 15 mA/cm^2 and 9% respectively.

The present paper deals with HAP coatings on the surface of 316L SS substrate by the direct as well as pulsed current electrodeposition method with hydrogen peroxide as an additive into the electrolyte. The influence of hydrogen peroxide concentration on the purity, phase composition and morphology of as-deposited coatings was also investigated and optimized appropriately. The impact of pulsed parameters such as peak current density, pulse on and off time on the crystallinity, morphology and adhesiveness of HAP coatings deposited on the 316L SS substrate was verified and compared to the continuous current density. In the present study, the current densities and the concentrations of H_2O_2 used for the deposition of HAP were much lower than the previously reported one [36]. To the best of our knowledge, so far there is no report on pulsed electrodeposition of HAP on 316L SS with H_2O_2 into the electrolyte.

2. Experimental procedure

2.1. Preparation of 316L SS specimen

Stainless steel substrates (purchased from Steel Authority of India, Salem, Tamil Nadu, India) whose elemental composition (wt.%) is C—0.0222, Si—0.551, Mn—1.67, P—0.023, S—0.0045, Cr—17.05, Ni—11.65, Mo—2.53, Co—0.136, Cu—0.231, Ti—0.0052, V—0.0783, N—0.0659 and the rest Fe were used as cathode for electrodeposition. The substrates are cut into dimensions of 1 cm × 1 cm × 0.3 cm and embedded in epoxy resin with a working area of 1 cm^2. Before deposition, their surfaces were abraded with different grades of SiC papers from 400 to 1200 grit to ensure the same surface roughness. The final polishing was done with coarse (6 μm) and fine (1 μm) diamond pastes in order to produce scratch-free mirror finish surface, and then degreased with acetone. This was followed by ultrasonic cleaning in acetone for 10 min and then the specimens were rinsed with deionized water, dried and used for further studies.

2.2. Electrodeposition of HAP on 316L SS

In this typical experimental procedure, the electrolyte was prepared by mixing a solution of 0.042 mol l^{-1} of $Ca(NO_3)_2*4H_2O$ and 0.025 mol l^{-1} of $NH_4H_2PO_4$ with varied concentrations of H_2O_2 such as 600 ppm, 1000 ppm, 2000 ppm and 3000 ppm. The electrolyte was de-aerated with N_2 for 30 min prior to and during the experiments. This is to reduce the amount of dissolved carbon dioxide and thus prevents the formation of $CaCO_3$ deposits. The pH value of the electrolyte was adjusted to 4.5 using dilute HNO_3 and NH_4OH. The temperature of the electrolyte was maintained at 65 °C by using an electric heater. Magnetic stirring was controlled at a speed of 180 rpm to keep the concentration of the electrolyte uniform. The electrodeposition was performed in an individual cell using a regular three electrode configuration in which 316L SS alloy served as cathode and a platinum electrode acts as an anode. Along with this, saturated calomel electrode (SCE) was used as the reference electrode. The deposition was carried out in galvanostatic mode using CHI 760C (CH Instruments, USA) by the direct and pulsed current electrodeposition methods. The current density was varied from 0.5 to 3 mA/cm^2 for the duration of 1 h. For pulsed electrodeposition as indicated in Fig. 1, a constant pulsed on time of $t_{on} = 1$ s with a current density of $j = 0.5$ mA/cm^2, 3 mA/cm^2 followed by the pulsed off time of $t_{off} = 1$ s, 2 s with $j_{off} = 0$ mA/cm^2