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Structural evaluation, preliminary *in vitro* stability and electrochemical behavior of apatite coatings on Ti6Al4V substrates

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ABSTRACT

Medical-grade alloys, such as Ti-6Al-4V, have been used for fixation of fractured bone and for the total replacement of defective bone. Their bioactivity could be improved by applying a bone-like apatite layer onto their surfaces. This, in turn, enhances their integration with the surrounding tissues upon implantation. In addition, the presence of a bioactive bone-like coating minimizes the likelihood of corrosion. Various methods are known for the formation of apatite coating onto Ti-6Al-4V, among which sputtering has shown its promise as a simple direct method. In the current work, a sputtering technique was used to develop a 300 nm-thick bone-like apatite layer onto Ti-6Al-4V. Structural composition, integrity and morphology of the as-coated and thermally treated coatings were investigated. Coated substrates were further evaluated after soaking them in a simulated body fluid (SBF) for up to 14 days. Results showed the formation of an amorphous apatite layer onto the alloy, that was further shown to partially crystallize upon heat treatment. As a result of SBF treatment, the apatite layer was found to remodel through a dissolution-precipitation mechanism due to its amorphous and non-stoichiometric nature, forming a smooth layer with better homogeneity and decreased surface roughness. Electrochemical analysis of the coated alloys showed the enhanced corrosion protection of the alloy surfaces by coating them with apatite. In addition, pre-grinding of the alloy surfaces before the formation of the coating was also found to improve the corrosion inhibition of the alloy surfaces in aqueous media.

1. Introduction

The most common trauma in road traffic accidents is bone fractures, in which bone fixation or replacement are considered the obvious avenues for orthopedic surgeons, especially in situations where the bone fracture is severe and cannot be cured by traditional bone cements [1]. For load-bearing bones, replacements with new biomaterials with comparable mechanical properties are the only resolution [2]. Several metals and alloys fulfill the mechanical requirements of the orthopedic prosthesis and fixation devices, such as medical grade stainless steel 316 L (ASTM F138) [3], Co-based alloys (mainly ASTM F75, and F799) [4,5] and titanium alloys such as Ti6Al4V (ASTM F67 and F136) [6,7]. However, only a few of them offer the required biocompatibility and corrosion resistance in the physiological medium [8]. It was found that these alloys do not develop a chemical bond with bone and wear and corrosion of the metallic implant over time can lead to the release of metallic particles causing different pathologies, including tissue irritation or inflammation [9,10]. This could finally end in the removal of the implant.

Approximately one-fourth of the commercially available medical devices is made of Ti-6Al-4V. This was attributed to the relatively higher biocompatibility of the alloy as a result of the formation of a passive, stable and continuous thin layer of the Ti and Al oxides onto its surfaces [11]. This has been thought to protect the underlying alloy from the aggressive environment in which it will be implanted. However, and despite the continuity of the oxide layer, it was found that it did not absolutely protect it from the release of Ti, Al and V ions into the surrounding body fluids [11].

To be used as a permanent replacement, an alloy has to chemically bond to the surrounding bone, a process that is usually defined as “Biological Fixation” [12]. This is defined as the process by which prosthetic components become firmly bonded to host bone growth or ingrowth without the use of bone cement [12,13]. As such, in the late 1960s, the concept of biological fixation of load-bearing implants using bioactive calcium phosphates, such as

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the bone-like hydroxyapatite ($Ca_{10-x}(HPO_4)_x(PO_4)_{6-x}(OH)_{2-x}$; HAp), was proposed as an alternative to cemented fixation [12]. Increasing the value of (x) in this composition and decreasing crystallinity of the apatite provides calcium phosphates that can be remodeled when exposed to body fluids through a mechanism of dissolution-precipitation [13]. This process allows HAp to form strong chemical bonds with natural bone and to promote new bone growth because of its similar chemical and mineralogical composition and crystallographic structure of apatite of human body living bone [14]. Pure HAp ceramics lack mechanical properties that allow them to be used for load-carrying applications [15]. Therefore, apatite coatings act as a barrier between body fluids and the metallic implant, and provide a surface on which bone can grow, forming chemical bonds at the bone/implant interface [16].

Since Furlong and Osborn first began clinical trials using the HAp-coated implants in 1985, it has been reported that HAp coatings can successfully enhance clinical success, and a less than 2% failure rate was reported during a mean follow-up study of 10 years [17]. One of the most widely used methods for coating biocompatible metals and alloys with HAp is the plasma-spraying process [18]. Despite its wide application for this purpose, there have been many problems indicating problems concerning the instability of the coating and the inability to control the structure of the coated layer [19]. As a result, numerous experimental deposition process have been investigated, including thermal spraying [20], pulsed laser ablation [21], dynamic mixing [22], dip coating [23], sol–gel [24], electrophoretic deposition [25], biomimetic coating [26], and hot isostatic pressing [27]. However, those techniques suffer from limitations like the lack of film homogeneity and the limited controllability of the film thickness. Radio frequency (RF) magnetron sputtering is a versatile deposition technique that produces thin, uniform, dense coatings that are homogeneous in structure and composition and they present good adhesion with the substrate [28]. In practice, sputter deposition is a method of depositing thin films by eroding material from a target material which then deposits onto a suitable substrate [29]. This process is driven by momentum exchange between the ions of an inert gas like argon (Ar) and atoms in the target material, due to collisions [29]. The incident ions set off collision cascades on the target. When such cascades recoil and reach the target surface with energy above the surface binding energy, an atom can be ejected [29]. It should be mentioned that apatite coatings produced using the sputtering process are known to be randomly deposited onto substrates as amorphous coatings [30]. Post-deposition heat treatments at various temperatures and heat treatments in a humidified environment were observed to induce the conversion of amorphous coatings to crystalline coatings, forming an apatite-type structure [30]. However, and due to the difference in the coefficients of thermal expansion of the apatite coating and the underlying alloy substrate, extended heat treatment may lead to shrinkage and possible detachment of the coating. Boyd et al. further explained the use of co-deposition sputtering technique to develop a Sr-substituted apatite coating onto a pure Ti substrate in order to enhance the osteoblast proliferation and differentiation, hence improve the overall biocompatibility of the coated substrates [31]. Therefore, sputtering method has an additional advantage of the ability to control the composition and crystallinity of the sputtered coatings by varying the post-deposition heat treatments. In the current study, a bone-like apatitic calcium phosphate coating has been developed on Ti-6Al-4V substrates that are pre-polished with different degrees. The effects of heat treatment and soaking in simulated body fluids on the structure and morphology of the coatings have been studied. Moreover, the electrochemical characteristics of the coatings have been investigated.

2. Materials and methods

A medical-grade cast, and annealed Ti-6Al-4V substrates were obtained from Good Fellow, USA, while commercial hydroxyapatite powder ($Ca_{10}(PO_4)_6(OH)_2$; HAp) was obtained from Sigma-Aldrich, USA. Substrates (10 mm in length, 10 mm in width, and 2 mm in thickness) were cut thereof and cleaned with soap and water followed by acetone for several times. As-received substrates were subjected to grinding using two different grades; namely P280, and P1200 grits. HAp powder was made into target disks (50 mm in diameter and 2 mm in thickness), followed by calcination at 800 °C for 1 h in air.

Sputtering of calcium phosphate coatings onto Ti-6Al-4V substrates was carried out using a Torr International Magnetron Sputtering System, USA. Sputtering conditions were pre-optimized to achieve a 300 nm homogeneous calcium phosphate coating onto the substrates, as indicated by the sputtering system program. Adhesion of the as-sputtered coatings to the underlying alloy surfaces was assessed by measurement of Brinell Hardness using a 1/16″ steel ball with the main load of 100 kgf. Values of the Brinell Hardness were expressed as BX values on the Brinell scale. Coated substrates were characterized for their crystallinity and surface composition using x-ray diffraction (XRD), Fourier-transfer infrared spectroscopy (FT-IR), and x-ray photoelectron spectroscopy (XPS), while their morphology and bulk composition were investigated using scanning electron microscopy (SEM) equipped with an energy-dispersive x-ray (EDX) unit. Coated substrates were further heat treated at 500 and 1000 °C, followed by characterization using XRD, XPS, and SEM-EDX techniques. XRD analysis was carried out on fully ground powders using a PW1840 diffractometer with a Cu K_a line at 1.5404 Å, an operating voltage of 40 kV and a 30 mA current generator. All samples were analyzed over a 2 theta (2θ) range 2–80° with a grazing angle of 2°. FTIR spectrum of the coated alloy was collected using a Nicolet Nexus 470 IR spectrophotometer, USA.

XPS analysis was conducted on a Perkin-Elmer PHI 5400 spectrometer equipped with a hemispherical electron analyzer and a non-monochromatic Mg Kα X-ray source (1253.6 eV). All reported photoelectron binding energies are referenced to the C 1s feature of adventitious carbon at 285 eV (internal standard) to take into account charging effects. The survey spectra were acquired at a pass energy of 178.95 eV. The detailed scan was performed at a pass energy of 35.75 eV. The measurements were performed following sputtering in Ar for 1 min to clean the surface. A selected region of the spectrum, that shows the spectra of the Ca and P elements, was scanned several times to obtain a good signal-to-noise ratio. Surface morphology of the coatings was investigated using a JEOL SEM at an accelerating voltage of 15 kV.

Preliminary *in vitro* evaluation of the coated substrates was carried out by soaking them in protein-free simulated body fluid (SBF) media for up to 14 days. SBF media were prepared following Kokubo's recipe [32] using proper reagents to produce media containing ions with concentrations shown in Table 1. Coated substrates were removed from the media after 3, 6, 9, 12, and 15 days of soaking at 37.4 °C. SBF-treated substrates were washed with DI water followed by acetone, then dried in air for 24 h.

Table 1
Concentrations of ions in SBF prepared in the current study compared with those of ions present in blood plasma [30].

	Concentration (mM)							
	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	Cl^-	HPO_4^{2-}	SO_4^{2-}
Blood plasma	142.0	5.0	2.5	1.5	27.0	103.0	1.0	0.5
SBF	142.0	5.0	2.5	1.5	4.2	148.0	1.0	0.5

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