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Electrochemical corrosion behavior of silver doped tricalcium phosphate coatings on magnesium for biomedical application

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ABSTRACT

This paper investigates the growth, characterization and electrochemical corrosion properties of tricalcium phosphate (TCP) doped with 0 wt%, 1 wt%, 5 wt% and 10 wt% of silver coatings deposited on magnesium substrate using pulsed laser deposition (PLD). The phase and morphological properties of the coatings were analyzed using X-ray diffraction (XRD) and scanning electron microscopy (SEM) respectively. The SEM images showed that increasing the percentage of Ag dopant reduces the size of droplets formed during the deposition process. The corrosion protection behavior of the coated samples was evaluated using potentiodynamic polarization (PD) and electrochemical impedance spectroscopy (EIS). The corrosion test was performed in Hanks' Balanced Salt Solution and 0.9 wt% saline solution using three electrode electrochemical cell. The results showed that TCP coated magnesium exhibits a much superior stability and lower corrosion rate compared to bare Mg. It was observed that increasing the mass of the Ag dopant increases the corrosion protection, but 10% Ag doping in TCP reduces the corrosion protection behavior. In conclusion, we have developed TCP and TCP doped with 1%, 5% and 10% Ag coating with tunable corrosion protection efficiency.

1. Introduction

Implant devices such as bone fixation plates, stents, screws, and wires are commonly used to provide structural support and/or to assist in the healing process after surgical procedures, such as orthopedic, craniofacial or angioplasty interventions. Presently, these implant devices are made from bioinert material such as titanium alloys, stainless steels and cobalt-chrome alloys [1–5]. However, additional surgeries are required to remove these devices once the healing process is complete [1,6]. This procedure increases cost and in some cases leads to patient morbidity [7]. In recent years, biodegradable metallic implants are beginning to change the paradigm of using only highly corrosion-resistant metallic implants for surgical procedures [8,9]. These biodegradable implants naturally dissolve *in vivo* after the healing process is complete and may not require second surgery. Even though polymers such as polyglycolic acid (PGA), polylactic acid (PLA), polydioxanone (PDS) have been widely used as biodegradable materials for certain applications, they lack the mechanical strength required for load bearing applications [10]. Biodegradable metals have more desirable mechanical properties due to their relatively high strength and fracture toughness [11–13]. Magnesium has shown great promise in this regard not only because of its high tensile strength and a Young's modulus which is comparable to that of natural bone, but its degradation products are easily metabolized by the body [8,14].

Although, magnesium is a great candidate for uses in orthopedic implant applications due to their biocompatibility, mechanical properties and degradability, they are susceptible to accelerated degradation in aqueous environment [15]. Recent research efforts have been geared towards the control of the degradation rate of magnesium by various surface modification processes and alloying with corrosion resistant elements [16–18]. Despite the recent progress in the effort to control the degradation rate, it is also important to consider the processes that take place between biodegradable implants and their surrounding tissues. Interface properties and interfacial processes between implants and their surrounding tissues in most cases determine the success of implants. Among the interfacial processes osseointegration and bacterial infection have been identified as the most pertinent in developing new materials and devices for implant applications [19,20]. Over the last two decades several research have dedicated a lot of effort to improve the osseointegration of implants by altering the chemical composition at the implant/surrounding tissue interface. The most reported materials commonly used are tricalcium phosphate and hydroxyapatite [21–24]. In addition to accelerating bone growth, tricalcium phosphate can improve the corrosion properties of magnesium. Zhang et al. (2009) reported that the corrosion rate of magnesium implants can be adequately controlled by covering them with well-adjusted thick apatite coatings [25]. Song et al. (2009) studied the transformation of β-

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tricalcium phosphate into uniform hydroxyapatite coating after immersion in 1 M NaOH solution. Their results showed a high improvement in the corrosion resistance and bioactivity on the surface of AZ91D magnesium alloy immersed in simulated body fluid (SBF) [26].

Another major risk associated with medical implant procedures is their high rate of infection at the implant-bone interface [19]. Silver coatings have been reported to exhibit excellent antibacterial properties capable of addressing bacterial colonization on implants and other nosocomial infections during surgical procedures [27]. The efficiency of silver coatings in controlling bacteria colonizing around an implant is dependent on the balanced of activities between the silver cation which kill bacteria and the concentration of silver ions released from the coating. A very high concentration of silver cations released from the coating can be toxic to cells [28]. Silver coating on magnesium will form a galvanic pair which will accelerate corrosion of the substrate. Therefore, doping TCP with silver can control the galvanic corrosion of magnesium, while enhancing the osseointegration properties. Also, the right balanced of silver is required to maintain the corrosion protection of TCP, as well as control the toxicity effect due to high concentrations of silver. Won-Hoon et al. (2007) investigated the antibacterial properties of Ag containing calcium phosphate coatings formed by micro-arc oxidation on titanium implants [29]. Their results showed that, while the coatings with a high content of Ag were cytotoxic, the calcium phosphate coatings obtained in the low Ag concentration electrolyte exhibited *in vitro* antibacterial activity but no cytotoxicity [29]. Although a lot of work has gone into improving the osseointegration and antibacterial properties of magnesium using TCP and silver respectively [30–32], there is the need to comprehensively evaluate the effect of Ag doped TCP coating on the corrosion properties of magnesium in simulated body fluids.

In the present work, we report the effects of Ag doping on the structure and corrosion properties of TCP coating developed on biodegradable Mg disk. The effect of different doping concentration on the microstructure and porosity were evaluated. The corrosion properties of the coatings were evaluated in Hanks' Balanced Salt Solution (HBSS) and physiological saline solution (0.9 wt% NaCl).

2. Experiment

2.1. Material fabrication

The β-TCP doped with 0 wt%, 1 wt%, 5 wt% and 10 wt% of silver coatings were deposited from in-house sintered target. The pure β-TCP (0 wt% doped Ag) target was prepared by cold pressing β-TCP powder (Sigma-Aldrich, USA) at 6×10^6 N/m^2 pressure followed by sintering at 1250 °C for 9 h. While the 1 wt%, 5 wt% and 10 wt% Ag doped β-TCP targets were prepared by mixing the pure β-TCP powder with the different weight percent of silver nanoparticles (Sigma-Aldrich, USA) followed by sintered at 850 °C for 9 h. The β-TCP doped with different compositions of silver coatings were deposited using a KrF excimer laser (Lambda Physik COMPex, $\lambda = 248$ nm and pulse duration of 20 ns). The laser was operated at a pulse rate of 10 Hz with energy density of 2 J/cm^2. The β-TCP doped with different weight compositions of silver coatings were deposited on Mg substrates at room temperature in vacuum in excess to 5×10^{-6} Torr (0.667×10^{-3} Pa). The deposition rate of the system was calibrated and the thicknesses of the β-TCP doped with different compositions of silver coatings were controlled at 1 μm. Polished high purity 99.97% Mg (Goodfellow, Germany) disks were used as substrates. The magnesium substrates were polished progressively with SiC paper from grade #400 up to grade #1200 using isopropyl alcohol as the lubrication fluid. The polished samples were etched in nital (methanol:nitric acid in the ratio 2:1).

2.2. Thin film characterization

The surface morphology and phase analysis of the films were investigated using Hitachi SU8000 scanning electron microscope (SEM) and Bruker D8 tool X-ray diffractometer (XRD) respectively. The SEM was operated at high magnification with a voltage of 2 kV and probe current of 5 mA. The XRD experiments were performed using a locked-coupled scan with a scanning range (diffraction angle, 2θ) set between 20 and 80°. The μ-XRF elemental analysis and mapping were conducted with 50 μm XGT capillary diameter with X-ray tube voltage and current of 50 kV and 1.000 mA respectively. The elemental analyses were conducted by selecting an array of 5 × 5 points (25 points) across the surface of the targets and coatings.

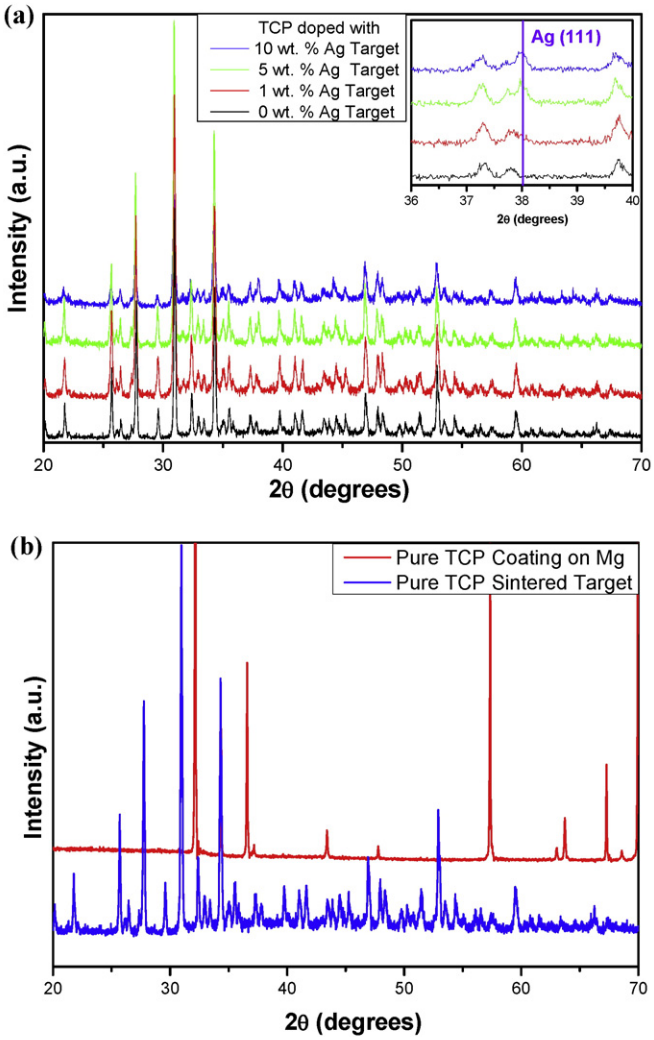

Fig. 1. (a) XRD pattern for sintered β-TCP doped with different compositions of Ag targets and (b) XRD pattern for sintered pure β-TCP target and pure β-TCP coating on Mg substrate.

2.3. Electrochemical test

DC polarization studies were carried out using a Gamry R600 Potentiostat (Gamry Instruments). All DC polarization measurements were performed in Hanks' Balanced Salt Solution (HBSS) and physiological saline solution (0.9 wt% NaCl) at room temperature. The scan rate was set at 0.5 mV/s spanning a scan range of ±0.3 V *vs* open circuit potential (E_{oc}). A Gamry para cell with a standard three-electrode configuration consisting of a standard Ag/AgCl electrode and platinum were used as the reference and counter electrodes respectively, while the sample acted as the working electrode. The working electrode was connected with a copper wire on the backside and installed in customized Teflon assembly and exposed on the solution side to about 0.283 cm^2 working