



Novel bi-layered nanostructured SiO₂/Ag-FHAp coating on biodegradable magnesium alloy for biomedical applications

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ABSTRACT

In this study, a novel bi-layered nanostructured silica (SiO₂)/ silver-doped fluorohydroxyapatite (Ag-FHAp) coating was deposited on biodegradable Mg-1.2Ca-4.5Zn alloy via physical vapor deposition (PVD) combined with electrodeposition (ED). The nano-SiO₂ underlayer had a compact columnar microstructure with thickness of around 1 μm while the Ag-FHAp overlayer presented large plate-like crystals accompanied with small rounded particles with thickness about 10 μm. Potentiodynamic polarization test exhibited that the double layer SiO₂/Ag-FHAp coated Mg alloy has superior corrosion resistance compared to uncoated and single layer SiO₂ coated samples. Contact angle measurement showed that Ag-FHAp coating over nano-SiO₂ layers significantly increased surface wettability which is favorable for the attachment of cells. Cytotoxicity tests indicated that the nanostructured SiO₂/Ag-FHAp coating enabled higher cell viability compared to nano-SiO₂ coating and uncoated samples. In addition, bi-layer and single-layer coatings considerably improved the ability of cell attachment than that of the uncoated samples. The cell viability of coated and uncoated samples increased with increasing incubation time. The double layer SiO₂/Ag-FHAp coated biodegradable Mg alloy possessed high corrosion resistance and cytocompatibility and can be considered as a promising material for implant applications.

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1. Introduction

Magnesium (Mg) and its alloys as a biodegradable materials have become an essential topic due to their low density, similar elastic modulus to human bone and good biocompatibility [1,2]. In addition, Mg alloys have higher mechanical strength compared to the biodegradable polymers and it is the cofactor for many enzymes and structure stabilizer of the DNA and RNA [3]. Without sufficient Mg²⁺ in the body, muscular paralysis, hypotension,

respiratory distress and cardiac arrest may occur [4]. However, the use of magnesium is hindered by its poor corrosion resistance which worsens the mechanical properties of the implant resulting in the inability of tissue to heal [5,6]. Furthermore, Mg corrosion process involves evolution of hydrogen gas which accumulates in vivo adjacent to the implant. The H₂ gas and subsequent formation of hydrogen bubbles can noticeably impair other clinical applications of magnesium [7,8]. To address this issue, high protection provided by the coating on Mg alloy is only for the initial stages of exposure to physiological media, however, as the exposure time increases, the coating becomes less effective. This kind of protection behavior over time is favorable for biodegradable implant materials since high initial corrosion resistance permits the implants maintain mechanical integrity until the injured tissues have had sufficient time to heal. Further increase in exposure time leads

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to implant is degraded as expected like bioabsorbable suture [9]. In this view, surface treatments such as plasma electrolytic oxidation (PEO), sol-gel process, laser cladding, ion implantation, micro-arc oxidation (MAO), anodic oxidation, atmospheric plasma spraying (APS), and polymer coatings are feasible methods for retarding the corrosion of Mg alloys [10]. Of these techniques, physical vapor deposition (PVD) is one of the most environmentally friendly methods for the protection of magnesium alloy [10,11]. In order to enhance the corrosion resistance of Mg alloy, PVD is used for coating of nano-SiO₂ as underlayer and electrodeposition (ED) for nanostructured Ag-FHAp coating as overlayer. This arrangement is advantageous because silicon is an essential ion in osteogenic cells with good biocompatibility and it improves corrosion resistance as well as it is beneficial to bone and cartilage, providing inertness to biological tissues [12,13]. Addition of the silica to the hydroxyapatite leads to noticeable enhancement of in-vivo bioactivity and early bone ingrowth [14]. In this regard, Kuo et al. [15] showed that SiO_x coating on AZ31 alloy significantly decreased corrosion current density and improved corrosion resistance. However, the presence of great amount of porosities in plasma coating leads to more absorption of the aggressive medium leading to more penetration of corrosive species to the substrate [16–18]. Therefore, several researchers [16,18,19] attempted to seal the micro-pores of plasma coating to enhance the corrosion resistance and bio-activity of the substrate. Hence, fluorine-doped hydroxyapatite (FHAp; Ca₁₀(PO₄)₆(OH)_{2-x}F_x, where 0 < x < 2) as overlayer was applied for this purpose and in order to form apatite [20,21]. FHAp presented good bioactivity, lower solubility in acidic medium and better biocompatibility than hydroxyapatite (HAp, Ca₁₀(PO₄)₆(OH)₂) [20,21]. Several researchers demonstrated that FHAp coating can improve corrosion resistance of magnesium and titanium alloys by providing protective layer on their surface [22–25]. It was suggested that doping of FHAp with some metal ions such as Ag⁺, Si²⁺, Cu²⁺, Ti⁴⁺ and Zn²⁺ leads to improved bioactivity and decreased risk of bacterial infection [26,27]. Among them, Ag⁺ presented oligodynamic property with no cytotoxic effects on human cells at low concentrations while it exhibited adverse effect at high concentrations [28,29]. In this view, doping HA with small amounts of Ag⁺ indicated good antibacterial activity with absence of cytotoxicity [26]. Liu et al. [29] showed that significant enhancement in the antibacterial property after incorporation of Ag in HA nanocomposite. Similar study [30] showed that the HA–Ag coatings on Ti alloy demonstrated higher antibacterial activity against *Escherichia coli* than that of HA coating. Yet another study [26] showed that Ag⁺-doped fluorapatite specimens exhibited high antibacterial activity against *Klebsiella pneumoniae*, *Staphylococcus aureus* and *Micrococcus luteus*. However, study on the biocompatibility and corrosion behavior of double layered nanostructured SiO₂/Ag-FHA coating on magnesium alloys could not be found in the literature. Therefore, in the present study, the PVD coupled with ED methods was utilized for the first time to prepare nano-SiO₂ coating as an underlayer and Ag⁺-doped FHAp coating as an overlayer on magnesium alloy in order to assess its potential for orthopedic applications.

2. Experimental procedures

2.1. Preparation of Mg-1.2Ca-4.5Zn alloy

Magnesium alloys were prepared by melting 99.9% pure magnesium ingots, pure zinc chip (99.99%), and Mg–32 wt% Ca in an electrical resistance furnace under protective gas atmosphere (60%Ar–40%CO₂). The crucible was held at a temperature of 760 °C for 30 min to melt the materials and further 15 min to allow for

homogenisation of the melt. Melts were cast in a 300 °C preheated mild steel mould coated with boron nitride. Subsequently, several Mg-1.2Ca-4.5Zn specimens were fabricated. The actual composition was determined by inductively coupled plasma (ICP). The ingots were then cut to provide specimens with dimensions of 15 × 10 × 10 mm. The specimens were then wet ground down to 2000 grit SiC paper to remove all visible scratches.

2.2. Preparation of nano-SiO₂ underlayer and nanostructured Ag-FHAp overlayer

A hybrid ion beam deposition system (HVC Penta Vacuum), consisting of a linear ion source and magnetron sputtering source with a SiO₂ target, was selected to deposit the coatings. The Mg alloys were ultrasonically washed in pure alcohol for 5 min before placement inside the vacuum chamber. An ion source with Ar gas was used to clean the surface of the Mg alloys for 40 min. This pre-treatment was performed when the base pressure of the chamber was below 2.55 × 10⁻³ Pa. Physical vapor deposition (PVD) was performed at room temperature with argon gas as the sputtering gas. The process used a sputtering pressure of 0.24 Pa, RF sputtering current of 200 W, deposition time of 90 min, and bias voltage of –150 V.

For coating of FHAp through the electrodeposition method, a conventional cell was fitted with a graphite rod as the anode and the Mg-1.2Ca-4.5Zn specimen (15 × 10 × 10 mm) as the cathode. The electrolyte was prepared at room temperature by dissolution of Ca(NO₃)₂ (0.042 mol/L), NH₄H₂PO₄ (0.025 mol/L), NaNO₃ (0.1 mol/L) and H₂O₂ (10 mol/L) at pH 5. The addition of 2 mM NaF to the electrolyte ensured a crystallized apatite structure in the FHAp coating. The FHAp coating was deposited at 60 °C and the current density was maintained at 4 mA/cm² throughout the electrodeposition for 1 h. The addition of NaNO₃ leads to an enhancement of the ionic strength. The pH value of the solution was adjusted to 5.0 by adding HNO₃ and (CH₂OH)₃CNH₂ at room temperature. In order to introduce Ag ions into the coating system, the FHAp coating was soaked in 100 ppm AgNO₃ (99.5% purity) solution at room temperature for 30 min to promote the exchange reaction of ions between Ag⁺ and Ca²⁺.

2.3. Corrosion testing and analysis

For electrochemical testing, rectangular specimens with a surface area of 1 cm² were mounted in epoxy resin, and the tests were conducted in an open-air glass cell containing 350 ml Kokubo Simulated Body Fluids (SBF) solution, using a PARSTAT 2263 potentiostat/ galvanostat (Princeton Applied Research). A three-electrode cell was used for potentiodynamic polarization (PDP) testing. The reference electrode was a saturated calomel electrode (SCE), the counter electrode was a graphite rod, and the specimen was the working electrode. The samples were immersed in the SBF solution for 1 h prior to the PDP test to establish the open-circuit potential. All experiments were carried out at a constant scan rate of 0.5 mV/s, starting at –250 mV relative to the open-circuit potential. The electrochemical impedance spectra (EIS) were measured over a frequency range of 1 Hz to 100 kHz using a VersaSTAT 3 machine. Each electrochemical test was repeated to confirm the reproducibility of the results.

Immersion testing was carried out according to ASTM G1–03 [31]. Alloy specimens with dimensions of 15 × 10 × 10 mm were immersed in a beaker containing 200 ml of Kokubo SBF [32] for 10 days. The SBF was not replenished during the testing period. The average pH value of the SBF from three measurements was recorded during the soaking experiment after an interval of 24 h. The immersion tests were repeated at least once to check the reproducibility of the results. After each immersion test, the samples

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