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Magnesium-sputtered titanium for the formation of bioactive coatings

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Abstract

Osteoconductive coatings may improve the clinical performance of implanted metallic biomaterials. Several low-temperature coating methods have been reported where a supersaturated solution is used to deposit typically apatitic materials. However, due to the very low solubility of apatite, the concentration of calcium and phosphate ions attainable in a supersaturated solution is relatively low (~1–2 mM), thus coating formation is slow, with several solution changes required to form a uniform and clinically relevant coating. In order to avoid this problem, we present a novel method where substrates were initially sputter coated with pure magnesium metal and then immersed in differing phosphate solutions. In this method, upon immersion the implant itself becomes the source of cations and only the anions to be incorporated into the coating are present in solution. These ions react rapidly, forming a continuous coating and avoiding problems of premature non-localized precipitation. The different coatings resulting from varying the phosphate solutions were then characterized in terms of morphology and composition by microscopy and chemical analyses. Upon immersion of the sputter-coated metals into ammonium phosphate solution, it was found that a uniform struvite ($MgNH_4PO_4{\cdot}6H_2O$) coating was formed. Upon subsequent immersion into a calcium phosphate solution, stable coatings were formed. The coated surfaces also enhanced both osteoblastic cellular adhesion and cell viability compared to bare titanium. The concept of sputter-coating a reactive metal to form an adherent inorganic metal coating appears promising in the field of developing rapid-forming low-temperature bioceramic coatings.

Keywords: Titanium coating; Magnesium sputtering; Struvite; Surface characterization; Osteoblast

1. Introduction

Metals have been the biomaterials of choice for biomedical load-bearing applications due to their combination of high mechanical strength and fracture toughness [1]. Hence, they are widely used as screws, plates, pins and implants (both orthopaedic and dental) where bone stabilization and/or augmentation are required. The current types of metals used are cobalt chromium (molybdenum) alloys, stainless steel 316L, pure titanium and titanium alloys [2].

Despite sufficient mechanical strength, metallic biomaterials have limitations that can be clinically detrimental. For instance, the elastic modulus of currently used metals is much higher than that of natural bone, and this can create stress shielding effects [3]. This is typified by increased bone resorption around an implant as a disproportionate amount of the load is taken by the metal rather than the surrounding bone. Since the peri-implant bone undergoes resorption, the implant may loosen and eventually fail [3]. Additionally, metallic surfaces have a limited capacity for integration with bone, which is determined by features such as surface topography and chemistry, and can release toxic ions through corrosion or mechanical wear [4,5]. This can stimulate an inflammatory response and subsequently loss of bone, which can lead to implant loosening [6,7].

Certain coatings on metallic biomaterial surfaces have been shown to improve corrosion resistance and improve the bioactivity of the surface through osteoconduction, i.e. bone ingrowth [8–10]. Several different coating approaches have been investigated to change the biological properties of metals and improve osteoconduction. These methods

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include plasma spraying of hydroxyapatite, alkali treatment of titanium surfaces to induce mineralization and direct precipitation of apatites in simulated body fluid [11,12]. Plasma spraying is the most commonly used method for coating metals [13]. However, this is a high-temperature process which limits the application to thermally stable coatings and substrates. Also, plasma-spraying does not allow for the coating of geometrically complex and porous surfaces [13]. Although aqueous deposition methods offer a solution to the limitations of plasma spraying, being a low-temperature coating process and able to coat any exposed surface, the technique is time consuming and yet to be commercially realized [14,15]. Alkali treatment of titanium [16,17] has performed well in vivo; however, the scope for varying surface and substrate chemistry is limited. Low-temperature coating methods are very attractive since they allow the incorporation of thermally unstable biologically active compounds such as growth factors, e.g. bone morphogenic proteins [18], adhesion molecules [19] and antibiotics [20] that may be used to improve the clinical performance of the metallic implant.

Traditionally, aqueous solution deposition of hydroxyapatite coatings is slow (in the order of days) [21]. This is due to the very low solubility of apatite such that the concentration of calcium and phosphate ions attainable in a supersaturated solution is relatively low (~1–2 mM). Therefore the solution's capacity to act as a simultaneous source of anions and cations is limited, slowing the deposition rate and requiring continuous renewing of the solutions [21]. We sought to avoid this problem by providing a source of cations on the metallic surface with which to react and form a calcium phosphate layer. To achieve this, the metallic substrate was first sputter-coated with pure magnesium metal, then immersed in differing phosphate solutions to effectively "pre-corrode" the magnesium before substituting the magnesium phosphate with calcium phosphate. Continuous coatings were formed rapidly therefore avoiding problems of premature non-localized precipitation.

Interestingly, magnesium phosphates may form pathologically in the human body and are found mainly in the form of struvite crystals ($MgNH_4PO_4{\cdot}6H_2O$) in kidney stones through the precipitation of trivalent phosphate in combination with ammonium ions [22–24]. Recent studies have exploited the biological importance of this mineral by suggesting a biodegradable and osteoconductive struvite-based cement for bone regeneration procedures [25]. However, despite promising reports, the magnesium phosphates remain relatively unstudied as bioceramics. This study investigated the use of sputter coatings of pure magnesium metal on titanium substrates as a solid phase reactant for the production of inorganic bioactive coatings.

2. Materials and methods

2.1. Magnesium sputtering of metallic substrates

Titanium sheet samples (6Al–4V alloy; 25.0 mm × 25.0 mm × 0.5 mm; McMaster-Carr Company, Los Angeles, CA, USA) were initially ultrasonically rinsed for 15 min in a 50/50 wt.% ethanol/acetone solution. Without any further pre-treatment, the titanium alloy sheets were sputter coated with the Denton Explorer®-14 sputter coating system with a 3 μm thick magnesium layer using 99.5 wt.% magnesium metallic targets (Goodfellow Cambridge Limited, England) of 20 cm diameter and a power of 150 W in high purity argon.

2.2. Coating of metals

In order to determine which solutions would be suitable for the formation of intact coatings, experiments were first performed by incubating the magnesium-sputtered titanium sheets in simulated body fluid solution (SBF) [26] and in an SBF where potassium phosphate was substituted for sodium phosphate (Table 1). Next, SBF components were examined individually to determine which, if any, were capable of forming a coating. The four that formed a coating, as determined by scanning electron microscopy (JEOL JSM-840A scanning electron microscope with an energy-dispersive X-ray (EDX) detector, both operating at 10–15 keV) were mixed in all permutations to examine the combinational effect on coating morphology. Only the three- and four-component combinations that produced any coating are presented in Table 1. The magnesium-sputtered samples were immersed in different precipitation solutions with a pH of 7.4 at 37 °C for 24 h (Table 1). In the case of struvite coatings, magnesium-coated samples were also immersed in ammonium diphosphate solution for 30 s and 2, 15 and 120 min, the reactions were arrested by immersing the samples in ethanol 100% and then vacuum dried before further characterization. Volumes (V_s; ml) for the immersion liquid were calculated based on the formula:

$$V_s = S_a/10$$

where S_a (cm^2) was the surface area of the sample as described previously [27].

All coatings that were rapidly soluble in both phosphate-buffered saline (PBS) and foetal bovine serum (FBS) were stabilized by immersion in a dilute calcium phosphate solution for 48 h (Table 1). The non-sputtered reverse side of the titanium sheets was used as a negative control.

2.3. Characterization of the coatings

All metal coatings were sputter coated with Au/Pd before being examined under scanning electron microscopy (SEM) coupled with energy dispersion spectroscopy at a potential of 10 kV and a working distance of 12.0 mm to determine their morphology and elemental composition. X-ray diffraction (XRD) and atomic force microscopy (AFM) analysis of the coatings were performed to evaluate their crystallographic nature and topology. A vertical-goniometer X-ray diffractometer (Philips model PW1710, Bedrijven b. v. S&I, The Netherlands), equipped with a Cu K_α radiation source, was used for the powder diffrac-

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