Applied Surface Science 416 (2017) 605–617

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Mechanical, structural and dissolution properties of heat treated thin-film phosphate based glasses

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ARTICLE INFO

Article history:
Received 12 December 2016
Received in revised form 6 April 2017
Accepted 15 April 2017
Available online 18 April 2017

Keywords:
Heat treatment
Phosphate glass
Mechanical properties
Ion leaching
Osseointegration
Thin films

ABSTRACT

Here we show the deposition of 2.7 μm thick phosphate based glass films produced by magnetron sputtering, followed by post heat treatments at 500 °C. Variations in degradation properties pre and post heat treatment were attributed to the formation of Hematite crystals within a glass matrix, iron oxidation and the depletion of hydrophilic P-O-P bonds within the surface layer. As deposited and heat treated coatings showed interfacial tensile adhesion in excess of 73.6 MPa; which surpassed ISO and FDA requirements for HA coatings. Scratch testing of coatings on polished substrates revealed brittle failure mechanisms, amplified due to heat treatment and interfacial failure occurring from 2.3 to 5.0 N. Coatings that were deposited onto sandblasted substrates to mimic commercial implant surfaces, did not suffer from tensile cracking or trackside delamination showing substantial interfacial improvements to between 8.6 and 11.3 N. An exponential dissolution rate was observed from 0 to 2 h for as deposited coatings, which was eliminated via heat treatment. From 2 to 24 h ion release rates ordered P > Na > Mg > Ca > Fe whilst all coatings exhibited linear degradation rates, which reduced by factors of 2.4–3.0 following heat treatments.

1. Introduction

Hydroxyapatite (HA) emerged as an osteoconductive coating in the 1980s and remains an industrial surface treatment for orthopaedic integration [1]. Second generation bioceramics facilitated interfacial bonding between the host tissue and implant [2]. Plasma sprayed HA is a ceramic coating layer with a Ca/P ratio of 1.67, similar in composition to the cortical bone. Bone like layers on metallic hip stems or dental screws promote adhesion of osteoblast cells and protein attachment for bone regeneration and osseointegration [3–5].

Plasma sprayed HA layers have been known to delaminate entirely at the interface, preventing complete osseointegration via the coating layer or causing integration directly with the implant surface. A study by Bloebaum et al. found particles of HA up to 75 μm, and metallic particles due to wear of the underlying implant embedded in the acetabular cup [6]. Despite improvements, aseptic loosening remains the biggest cause of implant failure, responsible for ≈40% of revisions [7].

The key factor for bioactivity is the stimulation of osteoblasts for collagen secretion and subsequent mineralisation of bone, assisted by creating an environment for osteoconduction at the surface of the implant device [8]. Collagen protein fibrils are laid down by osteoblast cells along the bone surface, facilitating regeneration from the creation of a extracellular matrix (ECM) [3]. Ca and P within the formed net of the ECM may mineralise to form crystallised bone in the form of HA. Phosphate Based Glasses (PBG) represent a third generation biomaterial which is fully resorbable in aqueous media and could repair the surrounding tissue by activating a controlled cellular response through the delivery of potentially therapeutic ions [1]. Research on PBGs has included Mg [9], Ca [10,11], Sr [12,13], F [14], which have been used for bone tissue generation, Ti [15–17], Fe [18,19] to improve durability, Cu [20] and Ag [21,22] for their antibacterial properties.

Pre-existing thermal technologies have been used to produce silicate based glass (SBG) coatings with mixed success. The inherent temperatures associated with the thermal processes, make the production of either adherent or amorphous glasses impractical without delamination, cracking or crystallisation. The thermal expansion mismatch leads to interfacial stresses and poor adhesion [23,24]. For example, Bioglass® 45S5 was plasma sprayed with failure occurring from thermally induced residual stresses at the Ti coating interface [25]. Bolelli et al. utilised suspension high velocity flame spraying [26] whilst Gomez-Vega et al. formed 25–150 μm thick coatings via an enamelling process [24].

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http://dx.doi.org/10.1016/j.apsusc.2017.04.110

Thin coatings in particular may be desired to prevent brittle failures associated with shear during implantation. A comprehensive review by Mohseni et al. concluded that magnetron sputtering produced the greatest interfacial adhesion of HA on Ti6Al4V after investigating 9 deposition methods including plasma spraying, hot isostatic pressing, thermal spray coating, dip coating, pulsed laser deposition, electrophoretic deposition, sol gel, ion beam assisted deposition and PVD sputtering [27].

RF magnetron sputtering of SBG was explored by Mardare et al. [28] and by Stan et al. [29]. The manufacturing complications associated with PBG coatings during sputtering has been demonstrated elsewhere [30], whilst a previous publication showed structural variability between compositionally equivalent melt quenched and PVD coatings, showing greater bulk and surface polymerisation in coating compositions [31].

The melt quenched PBG composition P_2O_5-40 MgO-24 CaO-16 Na_2O-16 Fe_2O_3-4 mol% (denoted MQ: P40) has been extensively researched for the production of degradable glass fibres [32]. Hassan et al. demonstrated good cytocompatibility with MG63 osteoblast cells, indicating comparable results to the tissue culture plastic control samples [33]. Therefore the work presented here investigates the sputtered coating composition; P_2O_5-40 MgO-24 CaO-16 Na_2O-16 Fe_2O_3-4 mol% applied to Ti6Al4V, specifically exploring the effects of surface topography and post deposition annealing on structural, mechanical, degradation and ion release properties.

2. Methodology

2.1. Target preparation T1: P51.5 Fe5 and melt quenched: P40

Pre-calculated (mol%) proportions of precursor salts namely sodium dihydrogen phosphate (NaH_2PO_4), calcium hydrogen phosphate ($CaHPO_4$), magnesium phosphate dibasic trihydrate ($MgHPO_4{\cdot}3H_2O$), iron phosphate dehydrate ($FePO_4{\cdot}2H_2O$) and phosphorous pentoxide (P_2O_5) (Sigma Aldrich, U.K.), were thoroughly mixed then preheated at 400 °C to dehydrate. The mixture was then melted in a Pt:Rh (90/10 wt%) crucible at 1200 °C for 2 h in air. The targets were formed by quenching the molten mixture at 450 °C followed by slow cooling to room temperature. The target mould and the subsequent target measured 75 ± 2 mm in diameter and 6 ± 1 mm in thickness. See Table 1 for target composition. MQ: P40 was similarly cast into 9 mm diameter rods and cut into 7 mm cylinders using a diamond saw.

2.2. RF magnetron sputtering

The coatings were deposited via a custom in-house designed Physical Vapour Deposition (PVD) rig using RF (13.56 MHz) magnetron sputtering, with a PBG target (denoted T1: P51.5). The chamber was pumped down to a vacuum using a combination of a rotary (Edwards E2M-18) and turbo molecular pump (Edwards EXT250) to a base pressure $<7 \times 10^{-3}$ Pa. Phosphate glass deposition was performed at 60 ± 1 W power (13.6 kW m^{-2}) for 1165 min to a coating thickness of 2.67 ± 0.09 μm at a pressure of 10 ± 0.05 mTorr of 99.99% pure-shield argon. The distance between target and substrate was also held constant at 4 ± 0.5 cm. Prior to deposition, targets were sputter cleaned for 30 min at 30 W and increased to 60 W for a further 30 min. The target glass has been labelled (T1), melt quenched glass rods as (MQ) and coatings as (C). Nominal compositions have been denoted by (N) whilst as prepared compositions assessed via EDX compositional analysis have been denoted by (AP). See compositions in Table 1.

2.3. Post deposition annealing

PBG coatings C2: P40HT30 and C3: P40HT120 were deposited as amorphous and subsequently heat treated in a Lenton tube furnace, with 99.99% pureshield argon to 500 °C at 10 °C min^{-1}. Coatings C2: P40HT30 and C3: P40HT120 were held for dwell times of 30 min and 120 min respectively. All samples were left to cool naturally to room temperature.

2.4. Thermo mechanical analysis

Thermal Expansion coefficient (TEC) was measured using Thermo Mechanical Analysis (TMA) via a TMA Q400. 50 mm long, 9 mm diameter MQ: P40 glass rods were heated up to 400 °C at a rate of 10 °C min^{-1}. The TEC measurements were obtained from a best-fit line between 50 and 300 °C. All expansion measurements represent the Standard Error Mean of $n = 3$ samples.

2.5. X-ray diffraction

Samples of the glass targets were ground to a fine powder for X-Ray diffraction (XRD) analysis (Bruker D8, Cu Kα source: λ = 1.5418 Å, 40 kV, 40 mA) conducted over a 2θ range from 15° to 65° with a step size of 0.04° in 2θ, and a dwell time of 5 s. In addition glancing angle XRD was performed on the deposited coatings utilising a step size of 0.02° in 2θ.

2.6. Energy dispersive X-ray spectroscopy

The compositions of the sputtering targets and sputtered coatings were determined via a Phillips XL30 SEM-EDX. Energy Dispersive X-Ray Spectroscopy (EDX) was conducted at a working distance of 10 mm at a minimum of 200,000 counts and a beam voltage of 15 kV. The electron beam current was optimised by increasing the spot size to obtain a minimum acquisition rate of 4000 counts s^{-1} whilst maintaining an acquisition dead time <30%.

2.7. Scanning electron microscopy

The coating cross sections and surface images were obtained via Scanning Electron Microscopy (SEM) using a Phillips XL30-ESEM. The working distance was kept constant at 10 mm, with a beam voltage of 15 kV. The precision of the EDX system was analysed over a repeated spot ($n = 5$), whilst coating homogeneity was assessed over ($n = 12$) random sample areas. Additionally, batch-to-batch variation ($n = 4$) was calculated and the estimated error is presented in Table 1.

2.8. Fourier transform infrared spectroscopy attenuated total reflectance

A Bruker Tensor Fourier Transform Infrared Spectrometer (FTIR) with an Attenuated Total Reflectance (ATR) attachment was used for all Infrared absorption measurements. A spectral resolution of 4 cm^{-1} over the wavenumber range 500–4000 cm^{-1} was set. All spectra obtained represent the average of 64 scans over the sample area.

2.9. Focussed ion beam scanning electron microscope

The coatings on Ti6Al4V substrates were sectioned and polished via a Focussed Ion Beam (FIB) using a Zeiss NVision 40 with a gallium milling source. The working distance was kept constant at 5 mm using a beam voltage of 5.00 kV. All sections were cut at a tilt angle of 54°.