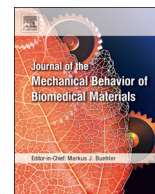




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Gallium incorporation into phosphate based glasses: Bulk and thin film properties



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ABSTRACT

The osteogenic ions Ca^{2+} , P^{5+} , Mg^{2+} , and antimicrobial ion Ga^{3+} were homogeneously dispersed into a 1.45 μm thick phosphate glass coating by plasma assisted sputtering onto commercially pure grade titanium. The objective was to deliver therapeutic ions in orthopaedic/dental implants such as cementless endoprostheses or dental screws. The hardness 4.7 GPa and elastic modulus 69.7 GPa, of the coating were comparable to plasma sprayed hydroxyapatite/dental enamel, whilst superseding femoral cortical bone. To investigate the manufacturing challenge of translation from a target to vapour condensed coating, structural/compositional properties of the target (P51MQ) were compared to the coating (P40PVD) and a melt-quenched equivalent (P40MQ). Following condensation from P51MQ to P40PVD, P_2O_5 content reduced from 48.9 to 40.5 mol%. This depolymerisation and reduction in the P-O-P bridging oxygen content as determined by ^{31}P NMR, FTIR and Raman spectroscopy techniques was attributed to a decrease in the P_2O_5 network former and increases in alkali/alkali-earth cations. P40PVD appeared denser (3.47 vs. 2.70 g cm^{-3}) and more polymerised than its compositionally equivalent P40MQ, showing that structure/mechanical properties were affected by manufacturing route.

1. Introduction

Phosphate Based Glasses (PBG) gradually resorb in aqueous media whilst releasing a custom array of ionic constituents making them desirable for potential biomedical applications, from resorbable composites for fracture fixation to therapeutic ion carriers (Ahmed et al., 2011). A Web of Science™ search for “phosphate glass” returned over 13,000 publications since 1984, when Bunker et al. reported on their dissolution capabilities in aqueous media (Bunker et al., 1984). To date, neither the U.S. Food and Drug Administration (FDA) nor U.K. Medicines and Healthcare products Regulatory Agency have regulated a single device containing PBG components. In comparison, the clinical applicability of 45S5 silicate based bio-glass developed by Larry Hench in 1969 obtained FDA (510 k) approval in six applications from 1985 to 2012. These included an Ossicular Reconstruction Prosthesis (1985), orthopaedic bone graft and toothpaste additives, known as Novabone (2000) and Novamine (2004), respectively (Hench, 2013). The research here developing orthopaedic glasses deposited as a multifunctional orthopaedic coating may for the first time enable utilisation on load

bearing materials and lead to a modern stratified approach to facilitating osseointegration, preventing bone degeneration or for combating infection around implant sites in applications which include total hip prostheses or dental screws (Stuart et al., 2015, 2017).

A PBG is composed of a three-dimensional covalent backbone (network) of tetrahedral PO_4^{3-} units bound together by P–O–P bridging oxygens or by multivalent non-bridging ionic constituents (Knowles, 2003). By convention the structure may be defined by the number of Q^n units within the glass, where $n = 0 - 3$, representing the number of bridging oxygens per tetrahedron (Knowles, 2003). Dissolution rates of PBG structures may be controlled by orders of magnitude by inclusion of intermediate elements such as Ti^{4+} , Fe^{3+} or Ga^{3+} which can either play network modifiers roles, depolymerising the glass structure through ionic cross linking or infiltrate and stabilise the backbone, creating hydration resistance through P–O–Ti, P–O–Fe or P–O–Ga type bonds (Neel et al., 2005a; Kiani et al., 2012a).

Ions including Ca^{2+} , Sr^{2+} , P^{5+} , and Mg^{2+} have been shown to stimulate osteoblast cell proliferation and differentiation towards mineralisation of regenerated cortical bone whilst the “potent”

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antimicrobial potential of Ga^{3+} was reported by Knowles and his co-workers (Hoppe et al., 2011; Valappil et al., 2008; Neel et al., 2005b; Ahmed et al., 2006). Valappil et al. reported on the positive efficacy of 1–5 mol% of Ga_2O_3 incorporated into a melt-quenched PBG composition (mol%: 45- P_2O_5 , 16- CaO , 34- Na_2O , 5- Ga_2O_3) against *Escherichia coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Clostridium difficile*. Ga^{3+} possesses the ability to inhibit bacterial development as similar atomic radii and equivalent trivalency lead to the bacteria's inability to distinguish between Fe^{3+} and Ga^{3+} known as the “Trojan Horse effect” (Kaneko et al., 2007). Microorganisms exploit the redox reaction of $\text{Fe}^{3+}/\text{Fe}^{2+}$ for electron harvesting (Weber et al., 2006). The inability to distinguish and reduce Ga^{3+} starves the cell resulting in apoptosis (Kaneko et al., 2007).

Stan et al. and Stuart et al. utilised Radio-frequency Magnetron Sputtering (RFMS), a Physical Vapour deposition (PVD) method, to deposit layers ranging in thickness from 200 nm to 25 μm of silicate- and phosphate-based glasses respectively onto pure titanium (Ti) and Ti alloy implant materials (Stuart et al., 2015; Stan et al., 2010a). PVD based technologies such as plasma spray (Cattini et al., 2014, 2013), pulsed laser deposition (Rau et al., 2012; Duta et al., 2014), or RFMS allows glasses to be applied uniformly to load bearing surfaces such as hip stems or dental screws to utilise their osteogenic and ion leaching potential. Furthermore, RFMS enables the fabrication of mechanically reliable films (Surmenev, 2012; Popa et al., 2015), fulfilling the requirements of ISO-137792 Part 2 “Coatings of Hydroxyapatite” (ISO, 2008) and the 1994 FDA draft guidance for Ca/P coatings on medical implants (Callahan et al., 1994), whilst process optimisation may supersede all reported methodologies with respect to interfacial adherence (Stuart et al., 2017; Stan et al., 2013). Its potentially low temperature (< 70 °C) operating conditions allows for deposition onto medical materials from metals to temperature-sensitive polymers (Dowling et al., 2001; Wolke et al., 1994).

The composition (mol%) P_2O_5 -40 CaO -16 MgO -24 Na_2O -16 Fe_2O_3 -4 has shown superior biocompatibility as an orthopaedic ion leaching glass due to the presence of 4 mol% Fe_2O_3 as a trivalent cross-linking and intermediate oxide (Hasan et al., 2012). To produce an antibacterial composition, Fe_2O_3 was replaced here by Ga_2O_3 (having a similar structural role), resulting in the P_2O_5 -40 CaO -15 MgO -24 Na_2O -15 Ga_2O_3 -6 formulation, labelled P40MQ or P40PVD, depending on the fabrication route. However, the effects of preferential sputtering lead to non-stoichiometric atomic transfer from the target material to the as-deposited thin film as discussed elsewhere (Stuart et al., 2016, 2015). In particular, a significant reduction in phosphorous (i.e., in the range ~11–15 mol%, depending on the sputtering parameters) has been found. Therefore, a target composition, richer in P_2O_5 , i.e. P51MQ, was sputtered to produce the P40PVD coatings. The primary aim was to evaluate the physical-chemical and mechanical modification as the glass is transferred from the melt-quenched target to the condensed thin film. Similarly the difference in properties between compositionally similar P40MQ and P40PVD is of great interest in future manufacturing and performance of implant glass thin films.

The secondary aim of the work presented here was to demonstrate the ability to incorporate osteogenic (Ca^{2+} , P^{5+} , Mg^{2+}) (Hoppe et al., 2011) and antimicrobial (Ga^{3+}) (Valappil et al., 2008) ions in quaternary PBG thin films onto medically relevant commercially pure Ti. The mechanical properties were assessed by nano-indentation. The majority of studies in the implant coatings area have focused on the identification of technological recipes capable of meeting the ISO standards and FDA requirements for the stipulated minimum pull-off adhesion of 15 and 50.8 MPa (ISO, 2008; Callahan et al., 1994) mandatory for load-bearing hydroxyapatite (HA) layers. This test, although useful for comparison is suboptimal due to the diversity of clinical failure modes. Therefore, due to the highly adherent nature of sputtered (hydroxyapatite and bio-glass) films, (Stuart et al., 2017; Popa et al., 2014), the elastic modulus and hardness properties were investigated by nano-indentation methods. This, in conjunction with detailed

characterisation through NMR, ellipsometry, IR and Raman spectroscopy and TEM allows a deeper understanding of the thin film coatings potential for clinical applications and insight towards the mechanical performance of an implant coating, as abrasion during implantation or *in vivo* micro-motion may lead to particulate spallation and aseptic loosening (Amstutz et al., 1992; Abu-Amer et al., 2007). Nano-indentation is commonly used to measure the elastic modulus and hardness of a test sample (Schuh, 2006), for example Leyland et al. used ratios of hardness to elastic modulus, obtained by nano-indentation measurements, to infer plasticity, toughness and abrasive resistance (Leyland and Matthews, 2000).

The collected information could serve as gauge for the potential of PBG coatings to be integrated in the design of a next generation of bio-functional implant structures.

2. Materials and methods

2.1. Substrate preparation

Substrates were 1 mm thick, 10 mm diameter discs of commercially pure Ti (cp-Ti, grade 1), wire-eroded from a sheet. Discs were first wet polished with abrasive SiC papers of different grit size (from P200 to P4000), followed by a final polishing stage using a 0.25 μm chemomet-finishing pad (Struers®) with the application of colloidal silica. The substrate roughness was measured as 4.2 ± 0.8 nm ($n = 5$ samples) by Atomic Force Microscopy over a scan area of $20 \times 20 \mu\text{m}^2$. Alternatively, double-side mirror polished Silicon (100) substrates were used for optical investigation of coatings.

2.2. Melt quenched glass fabrication

Pre-calculated (mol%) proportions of the glass precursors namely, Sodium Dihydrogen Phosphate (NaH_2PO_4 , Sigma Aldrich, St. Louis, MO, USA, purity > 99%), Calcium Hydrogen Phosphate (CaHPO_4 , Sigma Aldrich, St. Louis, MO, USA, 98–105%), Magnesium Phosphate Dibasic Trihydrate ($\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$, Sigma Aldrich, St. Louis, MO, USA, > 97%), Phosphorous Pentoxide (P_2O_5 , Thermo Fisher, Loughborough, UK, > 98%) and Gallium Oxide (Ga_2O_3 , Sigma Aldrich, St. Louis, MO, USA, > 99.99%), were thoroughly mixed in their powdered forms, then preheated at 400 °C in a Pt:Rh (90:10%) crucible for 30 min to dehydrate. For P51MQ production the mixture was then melted at 1200 °C for 2 h in air and subsequently quenched into a graphite mould to a target diameter of 75 ± 2 mm at 450 °C, followed by natural furnace cooling to room temperature. For P40MQ production the mixture was quenched into 10 mm diameter rods by the same protocol. Table 1 contains the nominal intended compositions for production of both Melt Quenched (MQ) and Physical Vapour Deposited (PVD) glasses.

2.3. Coating deposition process

Coatings were deposited via a custom in-house designed magnetron sputtering rig built at the University of Nottingham, utilising a 75 ± 2 mm, water cooled planar magnetron gun. The chamber was pumped down to high vacuum by combination of a rotary (Edwards

Table 1
Nominal sample compositions to produce MQ and PVD glasses. P51MQ was utilised as a sputtering target to condense P40PVD. The compositional equivalent of P40PVD, P40MQ, was produced for comparison.

	Oxide composition (mol%)				
	P_2O_5	CaO	MgO	Na_2O	Ga_2O_3
P51MQ	51.5	14.0	18.5	10.0	6.0
P40MQ	40.0	15.0	24.0	15.0	6.0

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