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Soda-lime glass-coating containing silver nanoparticles on Ti–6Al–4V alloy

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Abstract

The prevention and treatment of post-surgical infections is an ongoing concern. Post-surgical infections often cannot be treated with commercially available antibiotic-loaded bone cement as because higher doses of antibiotics are required. We describe here an approach to prevent implant infection through the use of glass coatings combined with silver nanoparticles deposited by sedimentation and heat-treated at 980 °C on titanium alloys. Silver is nontoxic to the human tissue and has been used as an anti-infective for centuries. The glass/silver coatings are composed of a soda-lime glassy matrix containing silver nanoparticles ranging from 2.6 to 20 wt.%. Optimum firing conditions have been determined for the fabrication of coatings that adhere well to the metal implant. These final coatings do not crack or delaminate. The biocidal activity of these coatings was also investigated. Coatings containing 20 wt.% of silver nanoparticles exhibited excellent biocidal activity ($\log \eta > 5$) against Gram+, Gram− bacteria, and yeast after 24 h.

Keywords: Titanium alloy; Silver nanoparticles; Glass; Biocide; Medical implants

1. Introduction

Medical implants are becoming more common in industrialized societies as their population sage and life expectancies increase. Around 25 million of Americans have at least one medical implant.[1] In 2003, more than 700,000 dental implant procedures were performed in the United States; more than 1.3 million were performed in Europe.[2] In 2006, it was reported that approximately 1 million artificial hips and knees were being implanted each year in the United States.[3] Hip and knee replacements have a success rate of more than 90%, and dental implants fare better, at 90–95%.[4] However, metallic implants are prone to infections following surgery and are significant cause of morbidity[5,6]; and billions of dollars are spent annually to treat infectious diseases. Infections of the implants, very often in the form of biofilm, are the most common of complications and occur in 1–4% of cases.[7] A biofilm is an accumulation of microorganisms (bacteria, fungi, etc.) and cannot be easily eliminated from an implant. Despite the availability of excellent (albeit toxic) antibiotics such as imipenem and tobramycin, a joint replacement infection will often require removal of the implanted joint.[8,9] Antibiotic-loaded cement is frequently used when revision surgery is necessary. However some clinicians have raised concerns about its cost, the risk of developing antibiotic resistant strains of bacteria, and the potential for long-term mechanical failure.[10–15] While the percentage of failure for dental implants is very low – approximately 5% – it is typically the result of infection, accelerated bone loss, or poor osseointegration with loosening of the implant.[4] Therefore, prevention of biofilm formation around dental implants is important, as it may cause periimplantitis, an infection that constitutes the most important risk for bone loss and affect the long time survival of the implants.[4]

Because of their high strength, hardness, and superior fracture and fatigue resistance, metallic materials such as Ti-based alloys, CoCr-based alloys, or stainless steel are presently regarded as

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the materials-of-choice for load-bearing implant applications. However, strong metallic implants have well-documented fixation problems and cannot self-repair or adapt like natural bone to changing physiological conditions. Metals have been shown to generate adverse host responses as a result of wear or electrochemical corrosion. Particle debris can provoke local inflammatory and osteolytic responses, while electrochemical corrosion may produce degradation products (e.g., metal ions) that may result in clinical failure of the implant or an undesirable systemic host response. The growing incidence of infections occurring after total knee or total hip replacement surgery requires novel and effective antimicrobials. The need for these is particularly great for prophylactic applications.

Silver has been used to treat infections for centuries and is considered nontoxic to human tissue. Silver ions are capable of killing a wide range of Gram negative and positive bacteria and strains commonly found following arthoplasty, including methicillin-resistant *Staphylococcus aureus* (MRSA) and other antibiotic-resistant bacteria. Surprisingly, the sequence of events and the mechanism(s) involved in killing bacteria with silver ions while sparing human cells are not well-understood. There is little scientific literature describing the use of silver coatings on implant surfaces to improve antimicrobial action, and most of it concerns the use of silver-loaded antibacterial bone cement.[16–19] New strategies to prevent infections are clearly needed. For example, it is possible to raise the antimicrobial activity of the current metallic dental implants through surface modifications either by applying novel ceramic coatings or by patterning the implant's surfaces with silver nanoparticles.[20]

The present work explores the feasibility of using glass, combined with uniformly distributed silver nanoparticles, as novel antimicrobial coatings on Ti implants. The glass/silver coatings are composed of a soda-lime glassy matrix containing silver nanoparticles in three concentrations: 2.6, 10, and 20 wt.%. The experiments were designed to evaluate the antimicrobial activity of these coatings, to determine their mechanical properties (adhesion to Ti6Al4V), and to optimize the glass/Ag compositions.

Our findings provide valuable insight into the biocidal behavior of the coatings, and pave the way for future work aimed at optimizing the biological and mechanical performance of such structures.

2. Materials and methods

2.1. Materials

The starting materials were (i) a commercial soda-lime glass from the SiO_2–Na_2O–K_2O–CaO–MgO–B_2O_3 system with the following chemical composition (wt.%): 70.2 SiO_2, 15.8 Na_2O, 7.1 CaO, 3.2 MgO 1.06, B_2O_3, 0.05 K_2O, 1.71 Al_2O_3, 0.02 Fe_2O_3, and 0.86 others with a deformation point ∼668 °C and (ii) vitellinate/nAg (Batch n° 127, ARGENOL S.L.), which is a protein of high molecular weight with a particle size distribution of $d_{50} \approx 10 \pm 2$ nm. This sample was fully characterized in a previous work[21] by differential thermal analysis (DTA), thermogravimetry (TG), X-ray diffraction (XRD), ultraviolet–visible absorption spectroscopy (UV–vis spectroscopy), and transmission electron microscopy (TEM). The chemical analysis was determined by inductively coupled plasma (ICP) and was found to be 20 wt.% of silver and 7.6 wt.% of sodium oxide.

In order to evaluate the role of silver in the wettability of the silver doped glass, silver free glasses with sodium oxide concentrations equal to the corresponding glassy matrices of the silver doped glasses were prepared as follows: (i) the glasses were prepared using reagent grade SiO_2 (Cuarzos Industriales S.A., Santiago de Compostela), α-Al_2O_3 (Taimei Chemical Co. Ltd., Japan), H_3BO_3, Na_2CO_3, and $CaCO_3$ (Sigma–Aldrich); (ii) the starting materials were mixed thoroughly and heated in platinum crucibles at 850 °C for 1 h to favour decarbonation of samples; and (iii) subsequently, they were melted at 1400 °C for 1 h, and then quenched into water. All the obtained glasses were found to be transparent.

2.2. Coating

Silver-doped glass powders with varying silver concentrations (2.6, 10, and 20 wt.%) were obtained following a similar procedure as that described in the previous work.[21] The soda-lime glass (<32 μm) and the corresponding fraction of vitellinate/nAg were homogeneously blended in isopropyl alcohol overnight under constant stirring at 30 rpm. After the suspensions were dried at 60 °C for 4 h, the homogeneous mixtures were uniaxially pressed into pellets (Ø ∼ 10 mm) at 250 MPa. Next, they were sintered in air in two steps; by heating at a rate of 3 °C/min to 500 °C and to 725 °C, respectively, and holding for 1 h. Tubular electrical furnace and zirconia crucibles were used. The obtained glass/nAg pellets were milled down to <32 μm in a planetary ball mill. These powders were fully characterized by XRD using a Bruker D8 diffractometer using CuKα radiation working at 40 kV and 30 mA in a step-scanning mode from 5° to 70° with a step width of 0.0288° and a step time of 2.5 s, by scanning electron microscopy (SEM) (Hitachi S-4300) and transmission electron microscopy (TEM) (JEOL FXII at 200 kV). Optical absorption spectrum was measured in a range from 200 nm to 800 nm, using a JASCO UV-Vis V-660 spectrophotometer to determine the surface plasmon resonance of silver nanoparticles.

Cladding of Ti–6Al–4V plates (99.0% purity and 12.5 mm × 8.3 mm × 1 mm) was performed by deposition of these powders (0.2 g), with a particle size distribution of $d_{50} = 11.56 \pm 0.03$ μm, from homogeneous suspension in acetone (20 mL) and subsequently air-dried at 40 °C. Afterwards, the coated plates were heated in an argon atmosphere at 980 °C for 1 h.

2.3. Characterization of the coating

The sessile drop method has been chosen to study the contact behavior between the titanium alloy substrate and the different coatings. Sessile drop experiments were performed on Ti–6Al–4V plates in an argon atmosphere at 980 °C for 1 h. For this purpose, pseudospheres (Ø ∼ 10 mm) were made by cold isostatic pressed at 150 MPa, using the same silver-doped