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In situ annealing of hydroxyapatite thin films

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Abstract

Hydroxyapatite is a bioactive ceramic that mimics the mineral composition of natural bone. Unfortunately, problems with adhesion, poor mechanical integrity, and incomplete bone ingrowth limit the use of many conventional hydroxyapatite surfaces. In this work, we have developed a novel technique to produce crystalline hydroxyapatite thin films involving pulsed laser deposition and postdeposition annealing. Hydroxyapatite films were deposited on Ti–6Al–4V alloy and Si (100) using pulsed laser deposition, and annealed within a high temperature X-ray diffraction system. The transformation from amorphous to crystalline hydroxyapatite was observed at 340 °C. Mechanical and adhesive properties were examined using nanoindentation and scratch adhesion testing, respectively. Nanohardness and Young's modulus values of 3.48 and 91.24 GPa were realized in unannealed hydroxyapatite films. Unannealed and 350 °C annealed hydroxyapatite films exhibited excellent adhesion to Ti–6Al–4V alloy substrates. We anticipate that the adhesion and biological properties of crystalline hydroxyapatite thin films may be enhanced by further consideration of deposition and annealing parameters.

Keywords: Hydroxyapatite; Pulsed laser deposition; Annealing

1. Introduction

According the American Academy of Orthopedic Surgeons, approximately 120,000 hip replacement operations are performed each year in the United States [1]. The high frequency of hip joint replacements can be attributed to the fact that loss of hip joint function produces such a severely handicapping condition. Problems with hips are related to the demands on the joint brought about by an upright posture for which evolution has not kept pace. Loads on hip joints as high as 1400 lb must be carried without plastic deformation or fracture. Prosthetic replacement of the hip is considered when the acetabulum or the head of the femur is damaged by degenerative or destructive conditions. These conditions include osteoarthritis, rheumatoid arthritis, ankylosing spondylitis, avascular necrosis, and persistent pain. The current implant design is based upon the pioneering work conducted by Sir John Charnley [2]. In these devices, a cobalt–chromium–molybdenum alloy (ASTM F75), cobalt–nickel–chromium–molybdenum alloy (ASTM F562), or a titanium–aluminum–vanadium alloy (Ti–6Al–4V) (ASTM F136) surface articulates against an ultrahigh molecular weight polyethylene (UHMWPE) surface. These components are fixed in place using polymethylmethacrylate (PMMA) bone cement.

Current devices have unacceptably short lifetimes. It is believed that 10–20% of the implants have to be replaced after 10 years, and some may need to be replaced in as little as 5 years [3]. Loosening, wear, corrosion, uneven stress distributions, and tissue inflammation contribute to these short lifetimes. The relatively poor longevity of these prostheses prompted Charnley himself to recommend that total hip arthroplasties be used only in older patients with limited life expectancies [4].

The polymethylmethacrylate bone cement presents many problems [5]. On one hand, bone cement assists in distributing stresses between the implant and the surrounding bone [6]. Unfortunately, micromotion at the implant–bone interface may lead to the release of a large amount of bone cement particles. In addition, stress concentrations at the implant/polymethylmethacrylate interface may lead to polymethylmethacrylate microfracture [7]. Metal, polymer, and bone cement debris can generate third body wear of the metal and polymer prosthesis components. Finally, these wear particles induce inflammation in the surrounding tissues, bone breakdown (osteolysis), and implant loosening.

Wear of orthopedic implant materials is another serious issue. A cobalt–chromium–molybdenum alloy/polyethylene

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implant generates a large number of polyethylene wear particles. Polyethylene wear is estimated at 0.10–0.20 mm/year; in fact, some investigators have suggested 100,000 polyethylene particles are released with each step [8]. Wear of the metal component of the joint prosthesis also occurs. For example, cobalt–chromium–molybdenum alloy degrades at an average rate of 0.02–0.06 mm in 10 years [9]. Titanium–aluminum–vanadium alloy is more prone to mechanical wear, especially at the titanium–aluminum–vanadium alloy/polyethylene interface [10]. On the other hand, cobalt–chromium–molybdenum alloy particles cause greater tissue toxicity than polyethylene particles or titanium–aluminum–vanadium alloy particles [11,12].

Stress shielding is another phenomenon that affects joint prostheses. This term refers to an uneven load distribution at the bone–prosthesis interface that can lead to prosthesis loosening [13]. This problem affects every current metal prosthesis component. For example, cobalt–chromium–molybdenum alloy exhibits a modulus of elasticity of 220 GPa. This value is ten times higher than that of the surrounding bone (17 GPa); as a result, stress shielding is quite significant. An alternative metal component material is titanium–aluminum–vanadium alloy. This biocompatible, highly corrosion resistant alloy exhibits a modulus of elasticity of 110 GPa. Unfortunately, titanium–aluminum–vanadium alloy demonstrates poor wear resistance, and exhibits crevice corrosion when fixed using polymethylmethacrylate bone cement.

The best replacements for bone have characteristics that approximate those of natural bone. One approach to providing a strong, long-lasting adhesive interface between a bone replacement implant and the surrounding tissue involves the use of bioactive ceramics [14]. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$) is the most well known bioactive ceramic material used in medicine [15]. This mineral, along with fluorapatite (FAp, $Ca_5(PO_4)_3F$), monetite (M, $CaHPO_4$), tricalcium phosphate (TCP, $Ca_3(PO_4)_2$), tetracalcium phosphate (TTCP, $Ca_4(PO_4)_2$), and octacalcium phosphate (OCP, $Ca_8H_2(PO_4)_{6.5}H_2O$), belongs to a family of minerals known as apatites. These materials demonstrate similar structures (hexagonal system, space group, P_{63}/m), and possess the structural formula $X_3Y_2(TO_4)Z$. In nature, apatite compositions include X and Y=Ca, Sr, Ba, Re, Pb, U, or Mn (rarely Na, K, Y, Cu); T=P, As, V, Si, S, or CO_3; and Z=F, Cl, OH, or O. In medicine, apatites of interest possess X=Y=Ca, T=P, and Z=F or OH. In the case of hydroxyapatite, T=P and Z=OH. Hydroxyapatite is similar to the biological apatites that provide strength to the skeleton and act as a storehouse for calcium, phosphorus, sodium, and magnesium.

There are many techniques that have been used to create hydroxyapatite coatings on metallic implant materials. Dip coating, electrophoretic deposition, hot isotatic pressing, pulsed laser deposition, sol–gel processing, and sputter coating have been used to deposit hydroxyapatite coatings; however, thermal spraying remains the most common commercial technique [16]. There are several problems with conventional thermal sprayed coatings. For example, hydroxyapatite is restricted from use in weight-bearing implants, because delamination of the hydroxyapatite film is a common problem. Failure of the hydroxyapatite film can occur at three locations: (1) at the hydroxyapatite/bone interface; (2) between the lamellae in the coatings; or (3) at the hydroxyapatite/metal alloy interface. In addition, thermal sprayed hydroxyapatite films contain large numbers of defects, porosity, and cracks; cohesive failure is another possible failure mechanism.

Pulsed laser deposition has several characteristics that distinguish it from other growth methods and provide special advantages for the growth of chemically complex (multielement) and composite materials [17]. The advantages of this technique include congruent (stoichiometric) transfer of material, phase purity, deposition from energetic plasma, capability for reactive deposition, and capability for reactive deposition. However, there are problems associated with pulsed laser deposition of hydroxyaptite thin films. Previous work suggests pulsed laser deposition of fully crystalline hydroxyapatite thin films requires temperatures greater than 400 °C and deposition in an Ar/H_2O gas environment. Deposition at lower temperatures produces amorphous films, which resorb too rapidly to provide in vivo implant–bone bonding. In addition, films deposited by pulsed laser deposition using an excimer laser on Ti–6Al–4V substrates either at room temperature or at elevated temperature in inert gases show very poor adhesion. These difficulties have been attributed to softening of the Ti–6Al–4V substrate, and to the formation of an intermediate titanium oxide layer between the hydroxyapatite film and the Ti–6Al–4V substrate. Mechanisms for lowering the processing temperature must be found to allow PLD-grown hydroxyapatite films to become clinically relevant implant materials.

In this study, postdeposition annealing of hydroxyapatite thin films will be examined. High temperature X-ray diffraction was used to determine film microstructure during annealing. The adhesion properties of unannealed and annealed hydroxyapatite films were compared using microscratch adhesion testing. These novel hydroxyapatite thin films have many potential orthopedic and dental applications.

2. Experimental procedure

Hydroxyapatite powder (Sigma Aldrich, St Louis MO) was pressed using a hot press at 3000 psi to form 1-in. diameter targets. The targets were sintered at 1000 °C for 1 h in a helium atmosphere. Ti–6Al–4V (ASTM F136) stock alloy was cut into 2 mm × 1 cm × 1 cm pieces. Substrates were ground with 240–4000 SiC paper, and polished with 1-μm alumina paste. The polished samples were ultrasonically cleaned in acetone and methanol for 5 min each prior to deposition. Silicon (100) substrates (Silicon Quest International, Santa Clara CA) were cut from a 4-in. wafer into 2 × 2 cm pieces, and ultrasonically cleaned in acetone and methanol for 5 min each prior to deposition. The silicon wafers were etched in a 10% HF solution for 5 min to remove the oxide surface layer. Finally, the Ti–6Al–4V alloy and Si(100) substrates were mounted onto the substrate heater and loaded into the pulsed laser deposition chamber.