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Pulsed laser deposition of hydroxyapatite thin films on Ti–6Al–4V: Effect of heat treatment on structure and properties

G.P. Dinda *, J. Shin, J. Mazumder

Center for Laser Aided Intelligent Manufacturing, University of Michigan, 2216 GGB, 2350 Hayward Street, Ann Arbor, MI 48109-2125, USA

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Abstract

Hydroxyapatite (HA) is an attractive biomaterial that has been widely used as a coating for dental and orthopedic metal implants. In this work, HA coatings were deposited on Ti–6Al–4V substrates by laser ablation of HA targets with a KrF excimer laser. Deposition was performed at ambient temperature under different working pressures that varied from 10^{-4} to 10^{-1} torr of oxygen. The as-deposited films were amorphous. They were annealed at 290–310 °C in ambient air in order to restore the crystalline structure of HA. The coatings morphology, composition and structure were investigated by scanning electron microscopy, atomic force microscopy, energy-dispersive X-ray spectroscopy and X-ray diffraction techniques. Mechanical and adhesive properties were examined using nanoindentation and scratch tests, respectively. The stability of the HA coatings was tested under simulated physiological conditions. This study reveals that the combination of pulsed laser deposition and post-deposition annealing at 300 °C have the potential to produce pure, adherent, crystalline HA coatings, which show no dissolution in a simulated body fluid.

Keywords: Hydroxyapatite; Pulsed laser deposition; Coatings; Ti–6Al–4V; Biocompatibility

1. Introduction

Hydroxyapatite (HA; $Ca_{10}(PO_4)_6(OH)_2$) is the main chemical constituent of bone tissue (~70%). For this reason, it has been examined for several decades as a material for making biomedical implants [1]. HA has been widely employed in non-load-bearing implants, as a bioactive material with desirable bone response. However, due to the very brittle nature of bulk HA ceramics, these cannot be used as orthopedic devices that must withstand substantial forces during their expected lifetimes [1,2]. It is commonly accepted that these drawbacks can be suppressed by application of thin HA coatings on a biocompatible high-strength metal or alloy. Due to the favorable biocompatibility of HA and attractive mechanical properties of metallic structure, HA-coated titanium and titanium alloys have become some of the most promising implant materials for orthopedic and dental applications [3,4]. Ideally, the coating of HA over metallic substrates should be pure, crystalline and adherent to serve as an effective implant. The coating layer should also encourage bone tissue ingrowth and prevent the release of metal ions from the implant substrate. Moreover, for true biocompatibility, the coating surface must encourage the attachment of cells and their subsequent multiplication.

In the past decade or so, a variety of coating techniques have been employed to obtain HA coatings with desirable features, including plasma spraying [5,6], flame spraying [7], radio-frequency magnetron sputtering [8], ion-beam sputtering [9], electrophoretic deposition [10], electrochemical deposition [11] and combinations of these methods. Plasma spraying is the major method commercially available for the production of HA coatings. However, most of the above-mentioned coating techniques have severe limitations. For example, plasma spraying leads to crystalline or amorphous phases of different calcium- and phosphorus-related materials, such as tricalcium phosphate, tetracalcium

* Corresponding author. Tel.: +1 734 764 2159; fax: +1 734 763 5772.
E-mail address: dinda@umich.edu (G.P. Dinda).

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phosphate and related amorphous phases. Moreover, this method produces films with poor coating/substrate adherence, great porosity and lack of uniformity in terms of both morphology and crystallinity. To solve these problems, other alternative coating techniques have been suggested to produce improved HA coatings. However, all these techniques are not yet fully capable to produce pure, adherent and crystalline HA coatings. HA dissolution rates in physiological buffers increase with decreasing crystallinity [12]. Since it is desirable to have HA coatings remain on the metal surface until sufficient new bone regenerates, high dissolution rates are undesirable from the point of view of bone mineralization on the implant.

Recently, pulsed laser deposition (PLD) has proven to be a promising method to produce pure, crystalline and adherent HA coatings. In 1992, Cotell et al. first reported the PLD of HA films on Ti–6Al–4V substrates [13]. Since then, several studies have been performed under various atmospheres (Ar, O_2, H_2O and combinations of these) to produce ideal implants [14–21]. The PLD technique allows good control of crystallinity with different compositions and phases, and even with HA as the only phase. However, it has been commonly reported in the literature that PLD of pure and crystalline HA thin films requires higher substrate temperatures (usually 500–650 °C) under an oxidizing atmosphere containing water vapor [13,16,18]. In contrast, at lower temperatures (below 450 °C) PLD produces amorphous films, which resorb too rapidly into the body plasma. Under conditions of high substrate temperature and a water vapor atmosphere, it is evident that the Ti-based substrate surface will be oxidized prior to HA film growth [15]. Consequently, the presence of a titanium oxide layer at the HA–substrate interface leads to degraded adhesion of the coating to the substrate [15,22]. To overcome this problem and improve crystallinity and adhesion, post-deposition heat treatment of amorphous HA coatings produced by PLD at room temperature has also been explored. However, it has been reported that the amorphous-to-crystal transformation occurs at about 450 °C [17], which is not a low enough temperature to completely restrict oxidation of Ti or Ti-based alloys. Hence, there is continued interest in fabricating crystalline HA coatings at lower temperatures to avoid extensive oxidation of the substrate.

In this paper, we report the fabrication of pure, adherent and crystalline HA coatings by post-depositional annealing, at 300 °C, of amorphous HA produced by PLD at room temperature. The goal of this paper is to study the progress of the crystallization process of the amorphous HA coatings on Ti–6Al–4V and to optimize the processing parameters to produce adherent, pure and crystalline HA films.

2. Materials and methods

2.1. PLD system and coatings production

The PLD system used in this study is shown schematically in Fig. 1. The major components include a KrF excimer laser source, an ultrahigh vacuum deposition chamber equipped with a rotating target and a fixed substrate holder plus pumping systems. The PLD was performed at ambient temperatures in a stainless steel vacuum deposition chamber, initially pumped down to a residual pressure of 10^{-5} torr and then filled with oxygen to the different processing pressure (10^{-4}–10^{-1} torr). Commercially available sintered HA (Berkeley Advanced Biomaterials, Inc.) dense discs, 27 mm in diameter and 7 mm thick, were used as target materials. Rolled Ti–6Al–4V sheets ($20 \times 20 \times 0.5$ mm^3) were used as substrates. Prior to deposition, the substrates were mechanically polished with SiC paper (400–4000 grit size) and finished by polishing with a colloidal silica suspension (OP-U). The polished substrates were ultrasonically cleaned in acetone and methanol prior to deposition. Ablation was done with a pulsed KrF excimer laser (Lambda Physik EMG 201 MSC) beam of 248 nm wavelength, the pulse lifetime being 20 ns and the pulsation frequency 10 Hz. The laser beam was directed at an incident angle of 45° onto the HA target to a spot size of 3 $\times$ 1 mm so that the energy density was 3 J cm^{-2}. In order to avoid piercing, the target was rotated during the entire deposition process at a speed of 16 rpm. The evaporated material is deposited onto a substrate placed 4–5 cm in front of the laser spot on the target. The average ablation rate was about 1 Å per pulse. The number of laser pulses determined the desired film thickness, which was around 2.5 μm, corresponding to 25,000 laser shots.

In order to restore the initial crystalline structure, the amorphous films obtained by PLD were annealed for 4 h at the following temperatures: 290, 300 and 310 °C. The heat treatment was performed in ambient air in a horizontal cylindrical furnace. Both heating and cooling rates were 5 °C min^{-1}.

2.2. Structural and morphological characterization

Surface morphology and composition of the films were examined by scanning electron microscopy (SEM; Philips XL30 FEG SEM) equipped with an energy-dispersive X-ray spectroscopy (EDX) device. Atomic force microscopy (AFM; Nanoscope IIIa, Digital Instrument Inc.) was also used for quantitative analysis of the surface morphology of the coatings. The deposited HA samples were cut into approximately 1 $\times$ 1 cm pieces, mounted onto sample supports and imaged by AFM in contact mode at a scan rate of 1 Hz. In order to check the crystallinity of the as-deposited and annealed coatings, X-ray diffraction (XRD) analysis was carried out with a Rigaku rotating anode diffractometer using Cu K_α radiation at 40 kV and 100 mA. The coatings were scanned in the standard θ–2θ geometry from 10° to 50° with a 0.01° step size and 2 s dwell time.

2.3. Mechanical testing

The hardness and Young's modulus of the films were investigated using a nanoindentation system, Nanoindenter

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