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Wettability and kinetics of hydroxyapatite precipitation on a laser-textured Ca–P bioceramic coating

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Abstract

Surface-textured calcium phosphate coatings at four different length scales were synthesized on titanium-based alloys using a pulsed Nd:YAG laser system by a direct melting technique. The textures were obtained by varying the laser spot overlap with a change in laser traverse speed. Surface roughness measurements of the textured coatings carried out using a white light interferometer indicated a decrease in roughness with increasing laser scan speed. Wettability of the coated samples measured using a static sessile drop technique demonstrated an increased hydrophilicity with increasing laser scan speed. The influence of such textures and the associated surface roughness on the precipitation kinetics of hydroxyapatite (HA) during immersion in simulated body fluid (SBF) was the prime focus of the present paper. The mineralized samples obtained after immersion in SBF were characterized using X-ray diffraction, energy-dispersive spectroscopy and scanning electron microscopy to understand the kinetics of HA precipitation. The results thereafter confirmed that the precipitation kinetics of HA was strongly modulated by the varying surface roughness.

Keywords: Wettability; Kinetics; Hydroxyapatite; Laser; Ca–P

1. Introduction

Bone is a specialized hard connective tissue composed of an extracellular matrix (ECM), which is approximately two-thirds inorganic. This inorganic mineral phase consists primarily of calcium and phosphate ions, with traces of magnesium, carbonate, hydroxyl, chloride, fluoride and citrate ions [1]. Synthetic calcium phosphate (Ca–P)-based bioceramics possess bioactivity, biocompatibility, osteoconductive, nontoxic, noninflammatory and nonimmunogenic characteristics, and thus have received much attention as an artificial bone graft substitute material. However, due to their poor mechanical properties, such as lower fatigue strength and higher elastic modulus, in comparison with the human bone, these bioceramics cannot be used as bulk in the manufacture of load-bearing implants [2]. Synthesizing Ca–P based coatings on Ti-based alloys, however, is an area of active research as both the beneficial mechanical properties owing to the underlying titanium alloy substrate and the improved bioactivity due to the altered surface chemistry (presence of Ca–P) can be achieved by this process. Several coating methodologies have been studied by various researchers to date, including plasma spray [3], ion beam-assisted deposition [4], sol–gel-based coatings [5], pulsed laser deposition [6] and electrophoretic deposition [7].

The in vitro bioactivity of these ceramic coatings, assessed by the precipitation of a hydroxyapatite (HA, $[Ca_{10}(PO_4)_6(OH)_2]$; an apatite-like mineral) layer on their surface during immersion in simulated body fluid (SBF) has also been studied by several researchers [8–10]. Such precipitation of HA on the sample surface is beneficial as HA is a naturally occurring mineral component of the human bone lying alongside the collagen fibrils. Hence, this layer provides the appropriate surface chemistry and

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thereby acts as a bone bonding interface, where the cells can preferentially proliferate and differentiate into complex tissues such as bone. The kinetics of such precipitation from the SBF, a solution with ion concentrations and pH value similar to those of human blood plasma, has attracted the attention of a number of researchers as it is a process similar to biological mineralization [11,12]. The above technique also provides an alternate method for developing HA coatings on Ti-based alloys [2,13–15].

The various factors that might affect the kinetics of HA precipitation on a substrate material include, but are not limited to, (i) the pH of the supersaturated SBF solution; (ii) ionic concentrations of the SBF solution; (iii) the ambient temperature in which the nucleation is allowed to take place; (iv) the substrate surface chemistry and (v) the surface roughness of the substrate. Theoretical calculations of HA precipitation by Lu and Leng [12] demonstrated that a higher thermodynamic driving force is needed for the precipitation of HA than for the other metastable phases, such as octacalcium phosphate (OCP, $[Ca_8(HPO_4)_2(PO_4)_4{\cdot}5H_2O]$) and dicalcium phosphate (DCP, $[CaHPO_4{\cdot}2H_2O]$), that are usually present in supersaturated SBF. Their modeling results showed that the HA nucleation rate is significantly enhanced at higher pH and approaches the nucleation rate of OCP at a pH of 10. Their calculations also indicated that DCP does not nucleate in normal SBF although it is kinetically favorable, and only precipitates when the calcium and phosphate ion concentrations increase to higher than normal levels in SBF. Based on their models, the authors reported that the presence of carbonate or a deficiency of calcium in SBF can also affect the kinetics of HA precipitation considerably. Their results showed that a carbonate-containing and calcium-deficient HA is more thermodynamically favored than stoichiometric HA. The experiments by Valero and co-workers [16] proved that DCPs nucleate more easily at lower pH (5–6.5) than HA and OCP, while OCP nucleates more easily than HA at mean to high pH (7–8). Such a discrepancy in nucleation rate was attributed to the variation in kinetic coefficients of OCP and HA, which are smaller than that of DCP by 10 and 18 orders of magnitude, respectively, at pH 6.5.

The effect of reaction temperature (15–60 °C) on the kinetics of HA precipitation was studied by Cui and co-authors [17]. They reported that the HA precipitation is highly temperature dependent and the nucleation rate is faster at higher temperatures. Further, they also demonstrated that the temperature has a great influence on both the particle size and the morphology of the precipitated hydroxyapatite. Kondyurin and co-workers [9] studied the kinetics of HA deposition on three solid substrates (stainless steel, silicon and silica glass) modified by sequential implantation of Ca and P ions. Following the kinetic studies using Fourier transform infrared (FTIR) and Raman spectroscopy, they concluded that the speed of deposition was different on the three substrate materials. Ducheyne et al. [18] used a self-assembled monolayer technique to create amine, carboxyl and hydroxyl functional groups on oxidized silicon wafers, and then studied its bioactivity by immersing in a supersaturated SBF. From their studies they concluded that a hydroxylated surface provides appropriate surface chemistry and thereby enhances biomineralization compared to other surfaces. Two different treatment techniques (alkali treatment and radiofrequency plasma treatment) on titanium alloys were carried out by Layrolle et al. [8] to alter the surface chemistry and the surface roughness simultaneously, and thereby study its influence on biomineralization. From their results they concluded that the radiofrequency plasma-treated surface showed pronounced biomineralization compared to the alkali treated surface.

In all of the above studies, the kinetics of HA precipitation was understood based on the theoretical models or by experiments with two or more controlling factors. In the present case, however, we only studied the effects of surface roughness on wettability and the precipitation kinetics of HA. A direct laser-based melting technique was employed to achieve Ca–P coatings with controlled texture and surface roughness on the Ti–6Al–4V substrate. Here the intermittent delivery of pulses from a pulsed Nd:YAG laser was used to control texture by varying the spot overlap with change in laser traverse speed. The textured samples were then immersed in a supersaturated SBF solution and the precipitation kinetics of HA was studied using X-ray diffraction (XRD) and energy-dispersive spectroscopy (EDS).

2. Materials and methods

Substrate coupons of Ti–6Al–4V ($100 \times 50 \times 3$ mm) were cut from rolled sheets using an abrasive cutter. The cut coupons were then prepared for coating by initially polishing using a 30 μm grit silicon carbide emery paper followed by rinsing with acetone. Calcium phosphate tribasic ($Ca_5(OH)(PO_4)_3$) powder obtained from Fischer Scientific was taken as the precursor material. This precursor powder had a spherical morphology with a unimodal distribution in the range of 10–30 μm. The precursor was mixed in a water-based organic solvent LISI W 15853 obtained from Warren Paint and Color Company (Nashville, TN, USA). The mixed slurry was then sprayed onto the preheated (~50 °C) substrate coupons using an air-pressurized spray gun. The sprayed coupons were air dried to remove the moisture and a uniform thickness of 40 μm was maintained for all precoating deposits. Finally, the samples were scanned using a 400 W average power, JK701 model pulsed Nd:YAG laser to obtain a metallurgical bonding between the precursor and the substrate material. The laser was equipped with a fiberoptic beam delivery system to transfer the laser beam from the laser head to the material. The control panel for laser allows the control of pulse height, pulse width, pulse repetition rate and pulse shape. The lens assembly is equipped with a 120 mm focal length convex lens, which gives a spot diameter of approximately 240 μm at focus. The focused spot is kept at