

DIP-COATING OF CALCIUM HYDROXYAPATITE ON TITANIUM ALLOY (Ti-6Al-4V) AND STAINLESS STEEL (316L) SUBSTRATES

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ABSTRACT

Titanium alloy (Ti-6Al-4V) and stainless steel (316L) are two of the most commonly used materials in the manufacture of orthopaedic implants. To achieve better biocompatibility with bone, metal implants made of 316L or Ti-6Al-4V are often coated with calcium hydroxyapatite (HA) bioceramics. This paper is to describe a new dipping solution recipe used for HA coating. Sample characterization was performed by SEM and XRD.

INTRODUCTION

Chemically-precipitated HA ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) powders were first prepared by Hayek and Newesely in 1963 [1]. In this route of HA synthesis, a solution of calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) and di-ammonium hydrogen phosphate ($(\text{NH}_4)_2\text{HPO}_4$), of proper concentrations, were reacted with one another at high pH values in the presence of ammonium hydroxide (NH_4OH) [2-7]. HA powders prepared and used in this study were synthesized by the previously published method of Tas [8, 9], which was basically a modification of the route used by Hayek and Newesely [1]. The best use of HA in load-bearing orthopaedic applications was as a coating layer on one of the stronger implant metals. Uncoated metal surfaces are generally responsive to the tissues surrounding them, however, coating these surfaces prior to implantation, by some means, will be beneficial in speeding up of new bone formation. The study presented here is mainly focused on the development of recipes of suitable solutions for the dip-coating [10-12] of HA on either Ti-6Al-4V or 316L substrates by using chemically-precipitated calcium hydroxyapatite precursor powders.

EXPERIMENT

HA precursor powders used in the preparation of dip-coating solutions were synthesized as follows [13, 14]: a 3 mL aliquot of 0.1 gpl (gram per litre) methyl cellulose (Sigma Inc., Lot No: 73H0365) solution was mixed (to act as a dispersant) with 1440 mL of de-ionized water. 0.152 moles of $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99%, Merck, Darmstadt, Germany) was dissolved in the above solution. Then, 0.09 moles of $(\text{NH}_4)_2\text{HPO}_4$ (99%, Merck, Germany) was dissolved in the above solution. 115 mL of 24 vol% ammonium hydroxide (99%, NH_4OH : Birpa, Turkey) was added at once into the above opaque solution. The solution was heated and vigorously stirred at 60°C for 90 minutes on a hot-plate. The precipitates that formed were recovered from the supernatant in the form of a cream by vacuum filtering, via a Buchner funnel. Polyethylene glycol (PEG: Merck, Germany, Mol. Wt.: 15 000), gelatine (GEL: Riedel-de Haen, Germany), and glycerol (GLY: 99.5%, Birpa, Turkey) were blended with the ethanol (EtOH)-water mixtures containing the HA suspensions. The ingredients of the dip-coating suspensions (SOL) were mixed in water-cooled glass containers, by using a sonicator (TUD) probe with a tip surface area of about 1.3 cm² (Misonix, Inc., XLS-2015, NY).

Ti-6Al-4V or 316L strips had typical dimensions of 20 × 7 × 1 mm. These strips were first abraded with SiC papers in the grid range of 400 to 1200, followed by washing in distilled water. A belt-and-pulley-type apparatus has been built and used in this study for dipping the strips into the HA suspensions, and it had a two-way electronic switch to descend and ascend the substrates into (and out of) the dipping suspensions, at constant speeds in the range of 15 to 300 mm/min.

The coated substrates were heat treated in a PID-controlled horizontal tube (multifire) furnace (Alser, Model: Protherm-1250, Ankara, Turkey) with a flowing (4 L/min) N₂ atmosphere at 840 ± 3°C (2 h of peak soaking time), by using heating and cooling rates of 2°C/min. The heat-treated substrates were characterized by using scanning electron microscopy (SEM: JEOL, Model: 6400, Tokyo, Japan) and X-ray diffraction (XRD). To test the adhesive strength of the coatings, two steel cylinders 5 mm in diameter were attached to both sides of the coated strips by a thin layer of glue [12]. The adhesive strengths were then determined in a universal tester by measuring the tensile stress to break apart the cylinders from the strips.

RESULTS AND DISCUSSION

The HA precursor powders synthesized (as described elsewhere [8]) and used in this study yielded stable (against sedimentation) dip-coating solutions. The phase purity of these powders was checked by powder XRD. The as-precipitated powders (following drying at 90°C) were not amorphous but poor in crystallinity; however, further heating at higher temperatures (600°, 840°, 1050°, and 1200°C), in an air atmosphere for 6 hours, improved the crystallinity of the HA powders [8], and they were found to be single-phase HA.

The method of preparation of the HA dip-coating solutions has been described elsewhere [13, 14] in greater detail. Table 1 and Figure 1 show together the crucial details of the optimized solution preparation recipes. In the processing flow-chart of Figure 1, the ellipsoids represent the ultrasonic irradiation steps (by UD), whereas the numbers in the ellipsoids refer to the mixing time in minutes and the ultrasonic irradiation intensity (in Watts/cm²), respectively.

Table 1. Recipe of HA Dip-coating Solutions

SOL	HA (wt%)	H ₂ O (wt%)	EtOH (wt%)	PEG (wt%)	GEL (wt%)	GLY (wt%)
1	7.3	16.7	66.5	2.8	-	6.7
2	7.3	13.8	66.2	2.2	0.3	10.2

The dip-coating solutions reported above were both able to yield homogeneous and defect-free green coated layers on titanium alloy or stainless steel strips. These strips were dipped (and later withdrawn) into these solutions at a speed of 100 mm/min by using the electronically-controlled dipping apparatus. The most significant characteristic of the solution prescriptions in Table 1 and Figure 1 was that the green, coated metal strips could be

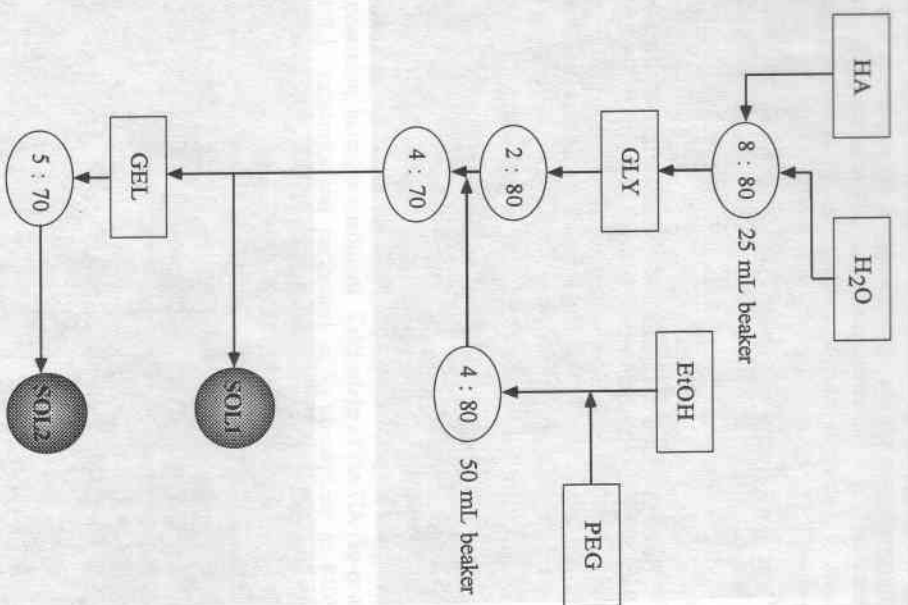


Figure 1. Process flowchart of HA dip-coating solution preparation

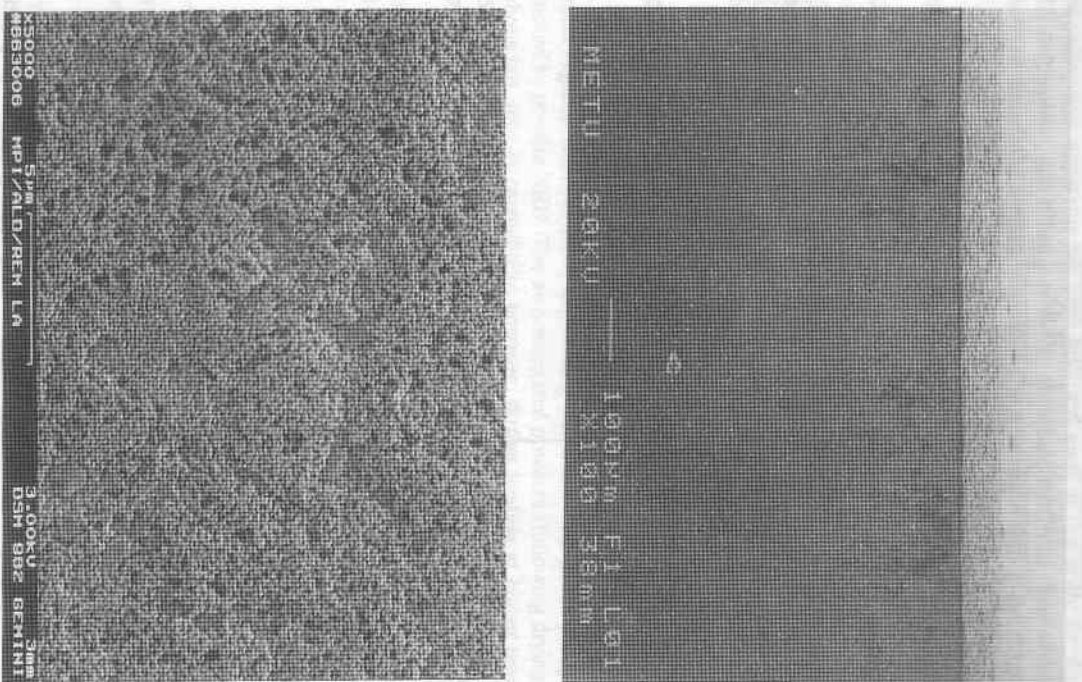


Fig. 2. SEM micrographs of HA coatings, after heating at 840°C; (top): cross-sectional view of the coat layer on Ti-6Al-4V strip, (bottom): porous microstructure of HA coat layer on 316L strip

immediately and rapidly dried in air at 90°C, without the need for controlling the humidity and the maintenance of slow drying conditions. The SEM micrographs given in Figure 2(a) and (b) exemplify the general appearance (on Ti-6Al-4V strip) and the microstructure (316L strip) of HA coatings, after calcination at 840°C in N₂ atmosphere for 4 h. The same crack-free and porous HA coatings were observed for both kind of metal strips used in this study. The HA particles seen in Figure 2(b) had an average particle size of ~ 0.25 μm. The dip-coating solution prescriptions presented here were able to produce a 55 μm-thick uniform HA layer on metal substrates at the stated dipping and withdrawal rate.

The glue used for adhesive strength tests were measured to have a tensile strength of 31 ± 2 MPa, and the breaks always occurred at a tensile strength value in this vicinity. It was thus concluded that the adhesive strength of HA coatings was larger than 30 MPa.

CONCLUSIONS

HA dip-coating solution recipes were developed to coat Ti-6Al-4V or 316L substrates. The organic additives used in these solutions consisted of polyethylene glycol, glycerol and/or gelatine. The dip-coating process was performed by using special apparatus which was able to provide constant (e.g., 100 mm/min) dipping and withdrawal speeds. The HA dip-coating solution recipes developed in this study did not require the drying of the green, coated metallic substrates under controlled humidity conditions. Calcination of the HA dip-coated metal (either Ti-6Al-4V or 316L) substrates was performed in N₂ atmosphere at 840°C. The coating thickness can be controlled by varying the solution HA concentration and dipping/withdrawal rates.

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STRUCTURAL AND CHEMICAL ANALYSIS OF CRYSTAL ENAMEL NUCLEATION

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ABSTRACT

The aim of the present study is to obtain structural and chemical information about nucleation and growth of dental enamel as a function of location in secretory mouse foetus enamel. Then enamel tissues were obtained from 19-days-mouse foetus. TEM images show that enamel crystallites had the well-documented thin ribbons, or needles. They were found in the outermost zone in the vicinity of ameloblasts. Chemical analysis by EDS showed that, besides the elements of hydroxyapatite, Na, Cl, Al and Mg are presents from the beginning of enamel mineralization. All of these elements will play an important role on the physics and chemical properties in mature enamel.

INTRODUCTION

Dental enamel proceeds from ecto-mesenchymal tissue and covers the anatomic crown of teeth. Ameloblasts are the secretory cells; their products are amelogenins, enamelin, tuftsin, proteoglycans, and enamel proteases. Mature dental enamel is formed by crystallites of hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$) (in 97%), organic material (1.5%), and water (1.5%) [1]. However, enamel hydroxyapatite is higher impure because of its readiness to accommodate foreign atoms in its unit cell [2]. Spectra of characteristic x-ray energy dispersive spectroscopy (EDS) of enamel crystallites showed the main components of the hydroxyapatite, excepting hydrogen. From these studies other elements, such as Na, Cl, and Mg, and some element substitutions, such as CO_3^{2-} , Mg^{2+} and F⁻ have been found in small quantities [1]. The crystallites are organized inside rods, or prisms, which are separated by organic materials. These prisms run at acute angles from the inner layer near enamel dentin junction to the surface of the tooth.

Transmission electron microscopy (TEM) images of enamel crystallites show a dark line of approximately 1.5 nm width along their centers whose contrast is focus dependent: it is dark underfocus, white overfocus and disappears in the exact focus value. This line has been named Crystal Dark Line (CDL) [3, 4]. The CDL has been experimentally observed in transversal and longitudinal human tooth enamel samples showing that it represent in reality a planar defect.

The origin of this CDL has had many interpretations, such as: anti-phase boundaries [5], structural defects linked to the initial growth process [4], lattice distortions, screw dislocations [6], grains boundaries, among others. It has been also indicated that it could be an initial precipitation of calcium phosphate thin ribbons and the subsequent epitaxial growth of hydroxyapatite. [7, 8]. This calcium phosphate is thought to be octacalcium phosphate (OCP). That is, that CDL is a remnant of a OCP layer for the nucleation and growth of hydroxyapatite enamel crystallites [8].