

CHEMICAL BATH DEPOSITION OF DICALCIUM PHOSPHATE DIHYDRATE COATINGS ON METAL SUBSTRATES

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Abstract: A novel and simple chemical bath method for deposition of dicalcium phosphate dihydrate (DCPD) coatings, otherwise known as brushite, has been developed. Precursor reactants for the chemical bath are aqueous solutions of sodium dihydrogen phosphate monohydrate and calcium chloride. Titanium alloy (Ti6Al4V) and stainless steel were used as substrates. The technique is based on multiple, dynamic chemical equilibrium reactions that provide a low precipitation rate. Successive depositions produced coatings up to 200 μm thickness, with microstructural variations influenced by surface treatment, solution concentration, stirring, substrate position, and deposition time. For example, coatings with variable grain size (a few microns to 400 μm), pore size (a few microns to 300 μm), and density, can be fabricated. This technique for deposition of DCPD is non-polluting, economical, and suitable for complex-shaped object of any size.

Keywords: Coatings, Dicalcium Phosphate Dihydrate, DCPD, Brushite, Bath Deposition

1. Introduction

Hexagonal calcium hydroxyapatite (HA), $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, and monoclinic dicalcium phosphate dihydrate, DCPD (otherwise known as brushite), $\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$, have been known to grow epitaxially on each other [1]. It has also been observed that DCPD is readily transformed into HA and fluoroapatite by chemical hydrolysis [2-5]. The phase transformation behavior of DCPD into HA, with the help of ultrasonic acceleration [6], as well as studies of additives on hydrolysis [7-11] have been explored. Additionally, bioactive DCPD coatings [12] have been prepared by electrodeposition [13,14] and from supersaturated solutions [15]. Although DCPD has not been detected in either bone or teeth [16], it is proposed to be a reactant for bone formation [1]. The latter study demonstrated that DCPD is an excellent apatite progenitor, which is more effective than stoichiometric hydroxyapatite in bone (incalvaria) reconstruction of rats.

This paper describes a novel chemical technique for deposition of DCPD coatings (~50-200 μm). Specifically, the chemistry, determination of the optimal growth conditions, and microstructures of these coatings are discussed.

2. Experimental procedure

2.1. Substrate preparation

The substrates used in this study were stainless steel (35 mm x 25 mm x 1 mm) and Ti6Al4V alloy (24 mm x 24 mm x 1 mm). The steel composition, determined by X-ray fluorescent spectroscopy, was found to be: 0.09% C, 0.25% Si, 0.32% Mn, 17% Cr, and 0.2% Ni. According to United Kingdom standards, this steel is designated as UK BS 430 S 15. Since the initial coatings exhibited poor adherence to the substrates, a sand blasting treatment of the substrate surfaces was performed. The substrates were then washed with soap in warm water, rinsed with deionized water, and dried in air.

2.2. Coating deposition and characterization

The DCPD coatings were deposited onto metal substrates in a chemical bath containing approximately 100 cm³ of solution. This aqueous solution was prepared by mixing equal volumes of calcium chloride (CaCl₂) and sodium dihydrogen phosphate (NaH₂PO₄), each having a concentration of 1-3 mol/dm³. Immediately following mixing, the substrates were either vertically supported against the walls of the beaker, or were suspended by a wire in the solution. The chemical deposition of DCPD was performed at various temperatures; the maximum temperature was approximately 40°C. The deposited materials were identified with the use of an X-Ray Rigaku diffractometer, model D/MAX-IIIB. All Infrared spectra were produced using a Perkin-Elmer System 2000 FTIR spectrophotometer (interferometer). Surface profilometry was performed using the Sloan Dektak II. A Mitutoyo Ultraplan FS-110 microscope with JVC TK 1280 U color video camera was used for the optical characterization.

3. Results and Discussion

3.1. Identification of coatings

Coatings were produced by four depositions. The phase identification and vibrational spectrum of the coatings were carried out using x-ray diffraction (XRD with Cu K α radiation) and Infrared Spectroscopy (FTIR), respectively. The XRD pattern (JCPDS # 09-0077) indicated the DCPD phase. The FTIR Spectrum of the powder, scratched off of the coating, confirms that the chemical composition is CaHPO₄ • 2H₂O.

3.2. Optimal growth condition

To determine the optimal growth conditions for the deposition of DCPD coatings, a series of experiments were carried out in which the temperature, reactant concentration, and parameters affecting the microstructure were varied.

3.2.1. Effect of Temperature

The temperature range, used to determine the upper limit for DCPD formation through precipitation, was 18 °C to 90 °C. The transformation of pure DCPD to pure monetite is observed. The mixed DCPD and monetite phases and semicrystalline monetite at an intermediate temperature range is clearly observed. The results indicate that phase-pure DCPD and monetite can be directly formed below 66 °C and above 68 °C, respectively.

3.2.3. Kinetic study

The time dependence of the mass of coatings (which is also proportional to the thickness) deposited at 18 °C and 40 °C, was determined as a function of reactant concentration. A steady state value of the mass indicated an end of the deposition process.

3.2.4. Parameters that affect microstructure

This study was carried out to determine the effects of substrate surface roughness, angular position of the substrate surface in the bath, and stirring on the thickness and microstructure of the coatings on Ti6Al4V alloy. The coatings were deposited, from an unstirred solution with a concentration of 2 mol/dm³, with the top edge of the substrates supported nearly vertical on the beaker wall. Note that the smooth as-received surface faced the beaker wall. A close inspection of the optical microphotographs reveals that the coating on the sandblasted surface has a higher grain size (from few to 400 microns), roughness, and pore size (from few to 300 microns), when compared to the coating on the smooth, reverse side. Additionally, the corresponding thicknesses of the coatings on these two surfaces were 227 μm and 130 μm, respectively. So the question of whether these contrasting features of the coatings were due to roughness of the substrate, or the angular position of the substrate surfaces (i.e., a given surfaces faces the wall, or is exposed to the bulk of the solution and at a small angle from vertical) remained open. However, further studies using substrate surfaces of different roughness (made by sandblasting followed by HF and HNO₃ treatments), coupled with a surface profilometry of the coatings, indicated that the latter was more important. In essence, a coating on a substrate surface (smooth or rough) facing the beaker wall, grew at a lower rate, and exhibited a microstructure with a smaller grain size and lower porosity. The rate of nucleation and growth of the coating probably dictated the final thickness for a given precipitation time. In contrast, surfaces facing the bulk of the solution, but resting on the beaker wall, developed thicker coatings probably due to enhanced sedimentation of precipitates. These coatings exhibited a microstructure with a higher grain size, porosity and roughness. For substrates held vertically in the solution, the microstructure was intermediate of the two aforementioned scenarios. Stirring the solution produced a microstructure with lower grain and pore size, higher density, lower growth rates, and thickness non-uniformity. Although stirring increases the precipitation rate, the coating growth rate is directed by the nucleation and growth at the substrate surface, because sedimentation on the substrate surface is suppressed.

The results of these studies indicate that the optimal concentration of the precursor reactants is 2 mol/dm³ with desirable reaction temperatures between 10-60 °C. If one desires to deposit a coating with a microstructure characterized by high porosity, and large grain and pore sizes, the processing parameters are as follows: reactant concentration of 2 mol/dm³ deposition temperature of 18 °C, and substrate surface exposed to particle sedimentation in an unstirred solution. Note that these conditions also give rise to thick coatings. Conversely, if a microstructure characterized by high density, and small grain and pore sizes is desired, the processing parameters are as follows: reactant concentration of 2 mol/dm³, deposition temperature of 18 °C, and substrate surface face the beaker wall so as to protect it from sedimentation in an unstirred solution. A microstructure with intermediate characteristics can be obtained from the same solution with appropriate stirring. Note that stirring reduces the rate of deposition and a low temperature allows the control of the chemical reaction.

4. Conclusions

A novel and very simple chemical bath technique for the deposition of dicalcium phosphate dihydrate coatings on sandblasted metal surfaces at room temperature has been developed. The technique can also be used for the deposition of CaHPO₄ (monetite) coatings. It was shown that the grain size, porosity, and pore size can be controlled by variations in the processing parameters. The thickness of the coatings can also be controlled from 50 to about 200 μm, with four successive two-hour depositions from a solution with 2 mol/dm³ concentration for both NaH₂PO₄ and CaCl₂. Additionally, with stirring at room temperature, dense coatings of 100 μm thickness can be produced on suspended substrates in solution. These kinds of coatings can be converted into hydroxyapatite coatings with the potential for medical applications. This potential application will be the driving force for future research.

Апстракт. Развиен е нов и едноставен метод за депозиција на калциум дихидрогенфосфат дихидрат (DCPD), познат како брушит. Хемиската бања се состои од прекурсорски водни раствори на натриум дихидрогенфосфат монохидрат и калциум хлорид. Слоевите беа депонирани врз супстрати од титанова легура (Ti6Al4V) и специјален челик.

Техниката се базира на реакција на динамичка хемиска рамнотежа којашто овозможува ниска брзина на хемиската реакција на таложење на брушитот. Со повеќекратна депозиција беа приготвени слоеви со дебелина до 200 μm, со микроструктурни варијации условени од површинскиот третман на супстратите, концентрацијата на растворите, мешањето, позицијата на супстратите и времето на депозиција. Методот овозможува приготвување на слоеви со различни големини на зрната (од неколку до 400 μm), како и варијации на дијаметарот на порите (од неколку до 300 μm). Оваа техника за приготвување на слоеви од брушит е незагадувачка, економична и соодветна за супстрати со сложена форма и произволна големина.

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