

## CHEMICAL METHOD FOR DEPOSITION OF MONETITE COATINGS

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**Abstract:** A new chemical technique for preparation of monetite coatings (anhydrous dicalcium phosphate) has been developed. The chemical bath consists of a solution previously used for deposition of dicalcium phosphate dihydrate (brushite) coatings. The coatings were deposited on sand blasted Ti6Al4V substrates as well as on stainless steel at 90-100 °C. A thickness of about 20 microns can be achieved from a single bath. The coatings were identified by X-ray diffraction analysis. Optical microscopy was used for thickness, grain and pore sizes determinations. An optimal concentration of 2 mol/dm<sup>3</sup> for both calcium chloride and sodium dihydrogen phosphate solutions for chemical bath deposition of monetite coatings was established by determination of the growth rate (deposited mass per unit surface, versus time). By a process of hydrolysis the prepared coatings can be easily transformed into hydroxyapatite which has potential applications for coating implants and prosthesis used in the medical field.

**Keywords:** monetite coatings, chemical bath deposition, anhydrous dicalcium phosphate

### 1. Introduction

Anhydrous dicalcium phosphate (DCPA) is found as mineral monetite, CaHPO<sub>4</sub>. It is classified in the triclinic crystallographic system. DCPA is one of the seven main calcium phosphate compounds that have a biological use as surgical materials [1]. It can be precipitated from a solution at above 70 °C and pH below 4 [1]. Monetite coatings have been prepared by a spray process [2,3] and were used for calcium hydroxyapatite coating preparation. The transformation of monetite coatings into hydroxyapatite coatings has been achieved by a process of hydrolysis. Formation of calcium hydroxyapatite as well as fluoroapatite has been a subject of other studies [4-10]. The idea of this paper is to present a new, simple technique for the preparation of monetite coatings as calcium phosphate precursors for fabrication of calcium hydroxyapatite coatings.

### 2. Experimental procedure

Stainless steel pieces (UK BS 302 S 17 and UK BS 430 S15) and Ti6Al4V pieces were used as substrates. Due to poor adhesion on smooth substrate surface, sand blasting was performed on the substrate surfaces. The diameters of sand particles used for sand blasting were from 80 to 200 microns. To clean the substrates from the sand dust, they were washed with soap in warm water, rinsed with deionized water and dried in the air.

## 2.1. Coating deposition and characterization

Monetite coatings were prepared in a 100 cm<sup>3</sup> beaker from a chemical bath containing a solution that was previously used for fabrication of dicalcium phosphate dihydrate coatings in our laboratory. Namely, calcium chloride solution with  $c = 2 \text{ mol/dm}^3$  and sodium dihydrogen phosphate solution with  $c = 2 \text{ mol/dm}^3$  were mixed in a volume ratio of 1:1 and used for dicalcium phosphate dihydrate coating fabrication at room temperature. After 4-5 hours of deposition the solution was separated from the precipitate and used for monetite coating preparation. The solution was placed in a beaker and the substrates were vertically suspended by a wire in the solution. Then the solution was heated up to 95 °C and kept at that temperature for 150 min. A terminal thickness of 20 microns was achieved from a single bath. Thicker coatings can be prepared by re-immersing the coated substrates into a fresh bath. The solution for chemical deposition of monetite coatings produces progressively less precipitate as the time passes and after ten or more days the solution is useless unless 3 g of urea are added to each 50 cm<sup>3</sup> of solution. Repeating this procedure, the waste solution can be used several more times by filtering it off and adding urea. At the end the waste solution is ammonium and sodium chloride.

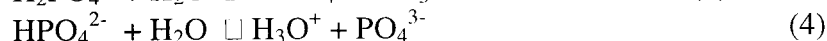
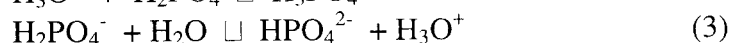
## 3. Results and Discussion

### 3.1 Chemical considerations

When solutions of calcium chloride and sodium dihydrogen phosphate with concentrations higher than 1 mol/dm<sup>3</sup> are mixed at room temperature, either slow or fast precipitation occurs depending on the concentrations. The precipitate is dicalcium phosphate dihydrate. At higher temperatures the chemical composition of the precipitate changes to an anhydrous phase known as monetite. The chemical deposition of monetite coatings can be described as follows:



However, the deposition process is in fact more complex. Dynamic equilibrium between several phosphate ionic species is involved:



The concentration of  $\text{HPO}_4^-$  ions depends on the concentrations of other ions as well as on the pH value. Low  $\text{HPO}_4^-$  concentration provides low reaction rate suitable for good coating growing conditions. During the deposition, a decrease of the pH value was noticed, due to  $\text{H}_3\text{O}^+$  concentration increase and the equilibrium reaction (3) shifts to the left, decreasing the  $\text{HPO}_4^-$  concentration and making the reaction rate much lower. When urea is added to the waste solution, in the course of the deposition process, the following hydrolysis reaction of urea occurs:



Due to its decreased solubility in acidic media as well as to the elevated temperature, the generated carbon dioxide is liberated as a gas. The gaseous ammonia will also have a decreased solubility, but in this case, it will immediately react with  $\text{H}_3\text{O}^+$  according to the following reaction:



This will decrease the concentration of  $\text{H}_3\text{O}^+$  and that in turn will affect the equilibrium described for the chemical reaction (3). The equilibrium will be shifted to the right, increasing the concentration of  $\text{HPO}_4^{2-}$  and allowing the deposition process to go further on.

### 3.2. Optimization of the composition of the chemical solution

Solutions of calcium chloride and sodium dihydrogen phosphate with concentration 1.5, 2 and 2.5 mol/dm<sup>3</sup> were mixed in volume ratio of 1:1. Namely, 50 cm<sup>3</sup> CaCl<sub>2</sub> c=1.5 mol/dm<sup>3</sup> and 50 cm<sup>3</sup> NaH<sub>2</sub>PO<sub>4</sub> c=1.5 mol/dm<sup>3</sup>, 50 cm<sup>3</sup> CaCl<sub>2</sub> c=2 mol/dm<sup>3</sup> and 50 cm<sup>3</sup> NaH<sub>2</sub>PO<sub>4</sub> c=2 mol/dm<sup>3</sup>, 50 cm<sup>3</sup> CaCl<sub>2</sub> c=2.5 mol/dm<sup>3</sup> and 50 cm<sup>3</sup> NaH<sub>2</sub>PO<sub>4</sub> c=2.5 mol/dm<sup>3</sup>. After four hours, the solutions were separated from the precipitates and they were used for kinetic studies. Sand blasted, stainless steel substrates were immersed in beakers with the solutions. Then, they were heated in a water bath up to 90 °C. During the deposition process, the coated substrates were taken out, rinsed with water, dried in a dryer and weighted. The mass of deposited material per unit surface was calculated. The dependence of the mass of the deposited material per unit surface versus time revealed that the deposition in the bath prepared from solutions with 1.5 mol/dm<sup>3</sup> ends after 70 min, for the one with 2.5 mol/dm<sup>3</sup> after about 100 min, while in the bath prepared from solutions concentration of 2 mol/dm<sup>3</sup> concentrations the deposition ends after about 150 min producing thicker coatings. The optimal concentrations for calcium chloride and sodium dihydrogen phosphate solutions are 2 mol/dm<sup>3</sup>.

### 3.3. X-ray and optical microscopy considerations

The X-ray diffraction pattern confirmed that the coatings were the expected anhydrous dicalcium phosphate. The analysis was performed by comparing experimental data with the JCPDS-ICDD diffraction pattern # 9-80 from PDF-2 set 1-46 Database. The peak at 2theta = 40.3 has a higher intensity than expected according to the standard. The increased intensity is probably due to reflections from the substrate. Infrared spectroscopy was also used for identification of the deposited material. Scratched powder from the coating was used for taking IR spectra with the KBr pellet method. The analysis of the wavenumbers and band shapes confirmed once again that the deposited material is DCPA (monetite).

The optical microphotograph of the surface of monetite coating reveals that the grain sizes have diameters from 30 to 65 microns and pore diameters from 10 to 50 microns.

## 4. Conclusion

The one key advantage of the described method is the use of a waste solution from a chemical bath deposition of brushite coatings. The proposed method is very simple and does not require any sophisticated equipment. This deposition technique can be used for any size and shape of substrates. The same bath can be used at least three times. Once for fabrication

of brushite coatings and two more times for preparation of monetite coating. It makes this method very economical. The monetite coatings can be turned into hydroxyapatite or fluorapatite coatings, and we are currently working on the details. The relatively high pore sizes of the coatings opens a potential for good bone ingrowth if these coatings were to be used as biocompatible material for coating bone implants.

**Апстракт.** Развиена е нова хемиска техника за приготвување на слоеви од монетит (калциум дихидрогенфосфат). Хемиската бања се состоеше од раствор којшто претходно беше користен за депозиција на слоеви од калциум дихидрогенфосфат дихидрат (брушит). Слоевите беа приготвени на супстрати од Ti6Al4V и специјален челик. Депозицијата беше изведена на температура од 90 до 100 °C. При една депозиција беа добивани слоеви со дебелина од 20 µm. Идентификацијата на тенките слоеви е изведена со помош на рендгенска анализа. За определување на дебелината на слоевите беше користена површинска профилометрија, додека пак за определување на дијаметарот на порите и зрната беше користена оптичка микроскопија. Врз основа на определената брзина на растење на слоевите, определена е оптималната концентрација на растворите од CaCl<sub>2</sub> и NaH<sub>2</sub>PO<sub>4</sub>, којашто изнесува 2 mol dm<sup>-3</sup>. Приготвените слоеви од монетит, по пат на хемиска реакција на хидролиза може лесно да се трансформираат во слоеви од калциум хидроксиапатит, со потенцијална примена за пресвлекување на импланти и протези користени во медицината.

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