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Functional Coatings Based on Hydroxyapatite and Polymers Formed on Ti-6Al-4V Substrates

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The paper describes perspective technology for deposition of inorganic-organic coatings used for biomedical application. Synthetic hydroxyapatite was used as inorganic compound, due to the similarity of the main component to bone tissue. As organic components we used chitosan and alginate – natural biopolymers, which widely used for bioactive and biocompatible composites formation. Thermal substrate method used for coatings deposition based on principle of decreasing solubility of hydroxyapatite with increasing of substrate temperature and allow to deposit coatings at substrate temperatures below 100 °C. Porous composite hydroxyapatite-chitosan and hydroxyapatite-alginate coatings were obtained on Ti-6Al-4V substrates. Morphology, phase composition and adhesion to the substrate surface were investigated.

Keywords: Hydroxyapatite, Chitosan, Alginate, Thermal substrate method, Composite coatings.

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1. INTRODUCTION

Metal ion release and bacterial infection of medical implants lead to inflammatory effects and infections in bone-implant interface in the physiological environment. That's why the application of bioactive coatings is very promising way to solve this problem. Polymeric materials are widely used in the field of medical implantology, due to their similarity to the physical-chemical properties of the living tissues which are mainly composed of biopolymers.

Chitosan (CS) and hydroxyapatite (HA) are among the best bioactive biomaterials in bone tissue engineering due to their excellent biocompatibility in the physiological environment [1]. Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is widely used in dentistry and orthopedics. It is one of the most thermodynamically stable forms of calcium phosphate which occurs in the bone as a major component (60 to 65 %) [2]. Chitosan is an alternative polymer using in orthopedic applications due to its good biocompatibility, biodegradability, porous structure, suitability for cell growth, osteoconduction and intrinsic antibacterial nature [3-5]. Chitosan is an N-deacetylation product of chitin. It is a copolymer consisting of β-(1 → 4)-2-acetamido-d-glucose and β-(1 → 4)-2-amino-D-glucose unit linkages [6].

Alginates – are the monovalent salts formed of alginic acid is a linear block copolymer composed of ß-D-mannuronate (M-block) and α-L-guluronate (G-block) linked by 1,4-glycoside linkage. [7] The G-block of alginate has correspondingly high affinities for divalent ions such as calcium (Ca^{2+}) at room temperature and thus in an aqueous solution of divalent ions, the alginate chains are rapidly cross-linked via the stacking of G-blocks to form gel [7].

In our work, nano-composite coatings consist of hydroxyapatite, chitosan and alginate were deposited by wet synthesis from aqueous solutions using thermal substrate method that allows obtaining coatings at temperatures below 100 °C which are favorable for final biomedical application.

2. MATERIALS AND METHODS

2.1 Materials

Ti-6Al-4V specimens, 36 × 1.9 × 0.36 mm in size, were used as substrates for CS-HA coatings deposition. They were first polished with sandpaper than washed in acetone (15 min) and 96 % ethanol (15 min) and in the end three times rinsed with distilled water under ultrasound. Biomedical grade chitosan (200 kDa molecular weight) was supplied by the Haidebei Marine Bio Ltd. (Jinan, China) with 9 % degree of the deacetylation. Solutions with various chitosan concentrations were prepared by dissolving the 1 g of chitosan fibers in 1 liter of 1 % CH_3COOH solution with vigorous stirring. Chitosan solution with concentration of 1 g/l was diluted to the required CS concentrations: 0.001; 0.025; 0.05; 0.1 g/l by mixing with the initial solution for HA synthesis which contains $CaCl_2$ (10 mmol/dm^3) and NaH_2PO_4 (6 mmol/dm^3). Sodium alginate with concentrations from 0.001 to 0.1 g/l was used for HA-alginate composite coatings formation.

2.2 Methods

The thermal substrate method for obtaining HA coatings based on the main principle that the solubility of HA in aqueous solution decreases with increasing substrate temperature [2].

Microstructure characterization and morphology analysis on the composite coatings were conducted using scanning electron microscopy (SEM), X-ray diffractometry (XRD), adhesion testing were studied by "tape-test method".

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Chitosan and alginate were inserted into hydroxyapatite coatings by the co-deposition onto titanium substrate from aqueous solutions having chitosan (alginate) concentrations of 0.001, 0.025, 0.05, 0.1 g/l under following conditions: substrate temperature 80-100 ºC, pH of the initial solution 6.5-6.8, time of deposition 180 min.

3. RESULTS AND DISCUSSION

Simultaneously, the following reaction of hydroxyapatite formation takes place on the substrate surface:

$$10Ca^{2+} + 6H_2PO_4^- + 14OH^- \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 12H_2O \quad (3.1)$$

The variation in coatings morphology is observed depending on the initial CS concentration in the solution (Fig. 1).

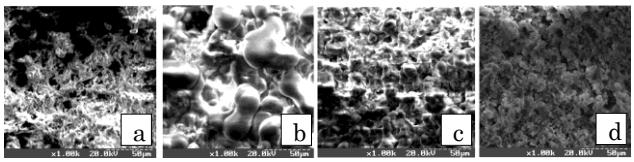

Fig. 1 – Morphology of the HA-CS coatings co-deposited by TSM method from aqueous solutions having chitosan concentrations of 0.1 g/l (a), 0.05 g/l (b), 0.025 g/l (c), 0.001 g/l (d)

For coatings obtained from solutions having CS concentrations of 0.001 and 0.025 g/l a homogeneous surface morphology is observed. The intensities of HA peaks are significantly higher for coatings having lower chitosan concentrations (Fig. 2) which can be explained by higher HA crystallinity.

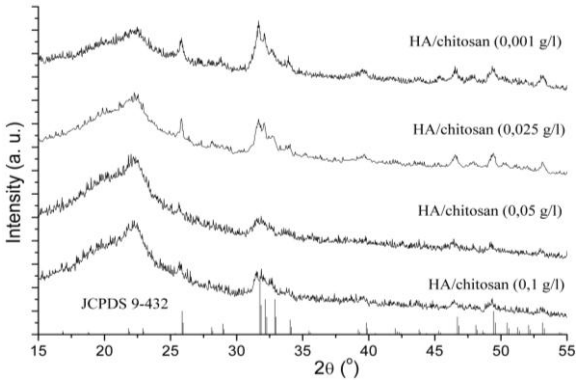

Fig. 2 – X-ray diffraction patterns of HA-CS coatings obtained by TSM from aqueous solutions with chitosan concentrations of 0.1 g/l (a), 0.05 g/l (b), 0.025 g/l (c), 0.001 g/l (d)

When chitosan is dissolved in acetic acid its amino groups are protonated (CS−NH3+) and bonds with carboxyl groups (CH3COO −) presented in solution. If other ions Ca^{2+}, HPO4 − are also presented in the initial solution some positively charged complexes for example CH3COO− −Ca^{2+} and HPO4− −Ca^{2+} can be formed in the solution. Such complexes can absorb negatively charged PO43 − with following crystal growth of HA. The presence of Ca^{2+} ions in the initial solution leads to chemical interaction between the calcium ions on HA surface and the amino groups in a chitosan molecule. In general, chitosan forms a chitosan-metal complex in which the metal ion coordinates the amino group in chitosan molecules. We suggest that small HA crystallites are able to align along the chitosan molecule upon aggregation through the interaction between the Ca^{2+} ions on the HA surface and the amino groups of the chitosan molecule. In other words, the c-axes of HA nano-crystals are parallel to the chitosan molecules due to formation of complexes of Ca^{2+} and amino groups of chitosan, which are the nucleation centers for HA crystals.

It has been observed that in preparing HA/alginate composites, Ca^{2+} ions present on the hydroxyapatite surface cross-link the alginate chains to produce a material with various morphology and adhesion to the substrate surface, both functions of the HA/alginate weight ratio. In vitro tests were performed on different samples in terms of both the HA/alginate ratio and synthesis temperature.

The results of adhesion testing by "tape-test" method show that HA-polymer coatings adhesion strength is greater than for simple HA coatings.

4. CONCLUSIONS

Composite coatings based on hydroxyapatite and natural polymers (chitosan and alginate) were deposited by thermal substrate method from aqueous solutions. The organic components affect the formation of HA coatings with various surface morphology depending on polymer concentration in the initial solution. Adhesion strength for polymer-HA coatings is also increased.

Following incorporation of antibiotics and antibacterial components into the matrix of CS or alginate can promote cell proliferation, faster and more efficient mineralization and bone formation.

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