A new approach to produce calcium-phosphate coatings on titanium

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Abstract. In the study, hydroxyapatite-gelatin composite powders were synthesized from simulated body fluid (SBF) with gelatin content ranging from 1 to 3 wt. %. It was established that all the samples were single-phase and represented hydroxyapatite. The surface and morphological characteristics of the produced hydroxyapatite-gelatin (HAG) based coatings were studied. Uniform deposition of the composite on the titanium substrate surface (VT1-0) was found to occur on etched titanium samples. It is shown that exposure of titanium substrates with hydroxyapatite-gelatin (HAG) based coating to powerful ion beam can stimulate further growth of crystals and regeneration of the surface.

1. Introduction

Titanium and titanium alloys are currently used to replace bone defects; however, in some cases, these materials are rejected by the human body, which leads to repeat operations, extended rehabilitation of patients and increased cost of operation. This problem may be solved through the formation of a bioactive calcium phosphate layer on a metal substrate. A number of methods are currently used to form these coatings, including calcium-phosphate deposition on smooth and structured surfaces of metals and alloys (current-free deposition, isostatic compression, electrophoresis, chemical vapor deposition, plasma spraying and etc.) [1–8].

The disadvantage of all the above methods is insufficient adhesion of the coatings to the metal substrate. Strong chemical bonding between the coating and the substrate can be formed through fusion temperatures 1073–1273 K, which results in a hard diffusion layer. However, mismatches between the synthesized surface of the material and the implant result in significant stresses that cause damage of the coating during cooling.

An alternative method is formation of biomimetic coatings on metals and their alloys [9–11]. In this case, the implant–bone bonding develops through the biomimetic formation of an active carbonate-hydroxyapatite (HA) layer on the material surface. This layer is formed as a result of the transition of calcium ions from the implant material into the fluid which composition is similar, as an example, to that of the simulated body fluid (SBF). Biomimetic apatite coatings may be formed on an inert material stable to dissolution, polymer as an example. This method has been successfully used for coating various polymeric materials, including the surface of fibers or fabrics. These can be used to make implantable structures, such as matrices for bone regeneration through cellular techniques. The imparted properties of these structures can be similar to those of the natural bone tissue, including high fracture resistance and low modulus of elasticity.

Initially, the biomimetic method was used to form apatite layers on bioglass and bioglass-ceramics, which in themselves are the source of calcium ions. This method was extended to polymeric and metallic materials. Hydroxyapatite based coatings are highly effective for osteointegration of metal implants in the bone. Titanium implants with these coatings are used in dentistry and orthopedics.

Thus, this formation of hydroxyapatite based coatings by biomimetic method stands out from the existing variety of methods to form a bioactive calcium phosphate coating on titanium and titanium alloys as a controversial one, and it requires further investigation. In this research, we aimed to produce a biomimetic gelatin-calcium-phosphate coating on the VT1-0 titanium alloy and to determine its composition and physicochemical properties.

2. Materials and methods

Hydroxyapatite was synthesized from the solution with a model medium close in its electrolyte composition to the human extracellular fluid [12]. During the synthesis, 500 ml of the K_2HPO_4, $NaHCO_3$, Na_2SO_4 and NaCl solution with the addition of gelatin was introduced into 500 ml of the $CaCl_2$ and $MgCl_2$ solution. The total volume of the mixture was 1 liter and the pH of the solution was 7.40 (with acidity correction error ± 0.05) with HCl or NaOH solution (20%). The crystallization time was 48 hours. After settling, the solution was filtered using a folded filter (blue ribbon). A portion of the supernatant was taken for chemical analyzes and the pH of the final solution was measured. After filtration, the filter cake was washed with water (V=50 ml) and dried in a drying box.

A VT1-0 grade titanium alloy was used for the study. This material has high tensile strength; it is highly biocompatible, non-toxic and corrosion resistant. Its characteristics are similar to the mechanical properties of the bone tissue. The surface of the samples was polished and etched; the etchant composition was HNO_3, NaF (1:1).

For deposition of hydroxyapatite on the VT1-0 titanium surface, 15 mm*15 mm*1.2 mm titanium plates were made. A part of the titanium plates was further exposed to powerful ion beam (PIB) and subjected to laser ablation.

Synthesis of the coatings on the plates for the HA system was performed in the presence of 1%, 2% and 3% gelatin. A hydroxyapatite suspension was prepared with the addition of gelatin, and then the titanium substrate samples were immerged in the suspension. The pH was 7.4, which corresponds to the physiological pH value.

The dependencies of the HA crystal growth and the coated surface areas for the VT1-0 titanium alloy with etched and untreated surfaces was studied by optical microscopy. The first observation was carried out after 3 day soaking in the solution, then observations were performed with an interval of 6 days. After applying the GA-gelatin layer onto the titanium plates, they were exposed to powerful ion beam using the “Temp” setup with the ion current density j=100 A/cm^2 and the number of pulses n=1.

To measure the limiting wetting angle, we used a technique based on measuring the geometric parameters of the droplets (diameter and height) of the liquid wetting the surface. The titanium sample surface was pre-degreased with ethyl alcohol solution, and a droplet of the suspension was released from a glass capillary with a diameter of about 0.2 mm on the surface. The geometrical parameters of the droplet were measured with a Neophot 2 optical microscope using a micrometer screw.

The phase composition of the prepared suspend was investigated by XRD (DRON-3) and IR spectroscopy (“FT-02” spectrophotometer). The peaks in the diffraction patterns were identified using the JCPDS card files and the software DifWin4.0 and Crystallographica Search-Match. The surface morphology was studied using optical microscopes Neophot 2 and MBS-9, and a scanning electron microscope JEOL JSM-6610LV.

3. Results and Discussion

HA were synthesized in the presence of 1 to 3 wt.% gelatin. It was found that when the gelatin content was 1 wt.%, HA crystallization was insufficient, whereas when the gelatin content was 3 wt.%, modified HA crystalline was formed that was identified by optical microscopy (figure 1).

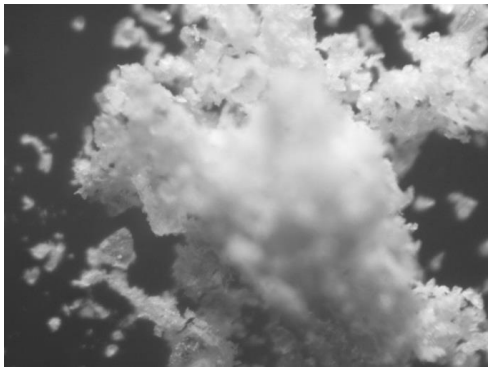
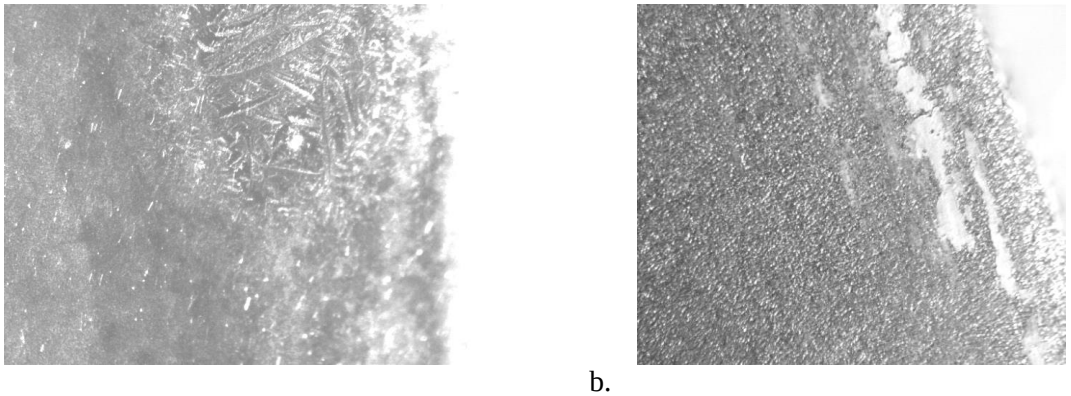


Figure 1. Crystallized HA powder in the presence of 3% gelatin solution (100x magnification).

As can be seen from the figure, the HA crystals formed in the presence of gelatin are of large sizes. The XRD results showed that the samples synthesized in the simulated body fluid under varying concentration of gelatin are single-phase and represent hydroxyapatite.

During formation of the coatings based on the synthesized composites (figure 2), dendritic crystals are seen to start growing on the plate edge.

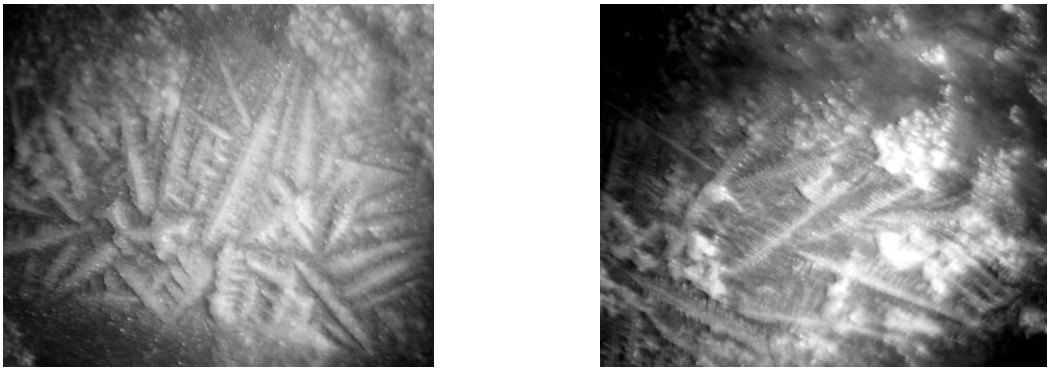


a. b.

Figure 2. Surface morphology of the hydroxyapatite crystals grown on the VT1 titanium alloy surface in the presence of gelatin after 3 day soaking in the solution: etched surface (a), polished surface (b) (100x magnification).

The crystallization rate was found to depend on the technique used for treating the implant surface. More rapid growth of crystals was observed in the microsections of the polished samples, whereas on the etched samples, dendritic growth occurred in bulk defects caused by etching.

The next observation of the titanium sample surface was carried out after 9 day soaking in the model solution. Figure 3 shows the surface morphology of the samples coated with hydroxyapatite during crystallization in the 3 wt.% gelatin solution.



a. b.

Figure 3. Surface morphology of the hydroxyapatite crystals grown on the VT1-0 titanium alloy surface in the presence of gelatin after 9 day soaking in the solution: polished surface (a), etched surface (b) (100x magnification).

As can be seen from the figure, dendrites continue to grow on both the etched and polished surface of the titanium alloy; the dendrites grown on the polished surface are thicker and shorter, whereas those grown on the etched surface are longer and thinner. In our opinion, this is related to different treatment of the sample surface. The crystallization is found to start in the direction towards the sample center, and the HAG coated area on the metal substrate is ~20%. As the crystallization period was increased to 18 days (figure 4), the coating layer thickness increased. On the etched surface, it was ~70 μm, and on the polished one, it was ~50 μm. It is significant that when the HA-gelatin suspension was changed after three days, the increment in the thickness value was 20 μm for each sample, which is characteristic of the mechanism when crystals grow on the surface of the biopolymer that had already been formed.

On the polished sample, the coating was loose, and it could be easily removed from the surface. On the etched surface, cracks were formed due to increased thickness of the resulting layer.

According to the results obtained by scanning electron microscopy (figure 4), in all the cases, the HAG -gelatin coating was formed with characteristic hexagonal crystal structure. A greater layer thickness resulted in cracking. After applying the HAG-gelatin layer, the titanium plates were exposed to PIB using the "Temp" setup. Figure 5 shows the morphology of the HA-gelatin layer on the sample surfaces after exposure to PIB. Under PIB action, high temperature gradients caused melting of the titanium implant surface layer and partial mixing of the HAG -gelatin layer and the substrate. In some places, the HAG layer disintegrated. In our opinion, it was due to non-uniform coating thickness. It was found that PIB irradiation of the coatings synthesized from the model solution in the presence of gelatin lead to fusion of the coating layer and its reliable adhesion.

This increases the biocompatibility of titanium implants, and crystallization of the HAG -gelatin composite on the sample surface may continue.

The results obtained by scanning electron microscopy (figure 6) show that some part of the HAG gelatin coating particles are in the form of rods. The sample structure is porous and it has microcracks that also cause further crystal growth and in vivo biodegradation.

The XRD of the coating (figure 7) indicated the reflexes of the original model – the VT1-0 titanium alloy, HA-gelatin composite and the sample after irradiation. After irradiation, HA peaks could be observed, and the structure of the titanium substrate surface was not modified. Thus, it can be noted that the exposure of the coating to PIB results in firm adhesion of the HAG –gelatin layer crystallized from the model solution on the titanium substrate. The coating produced by this technique can be used for implant manufacturing.

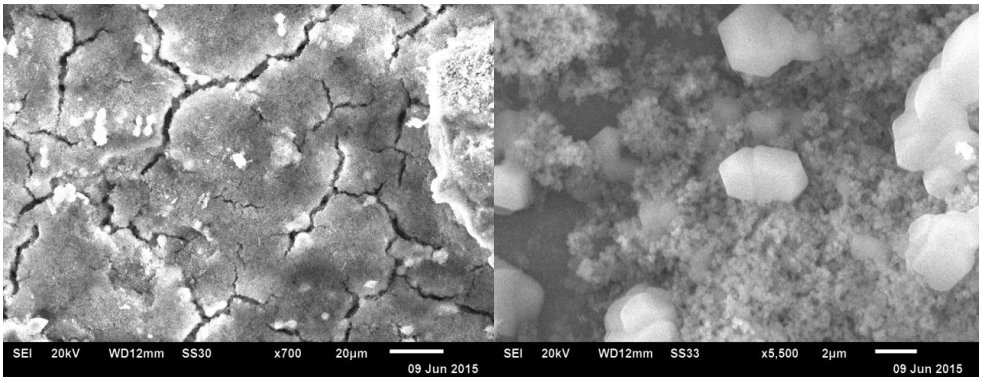
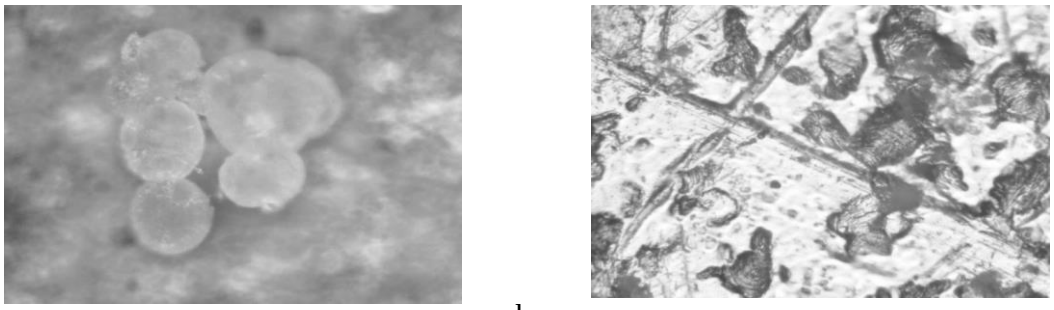


Figure 4. Surface morphology of the hydroxyapatite crystals grown on the polished surface of the VT1-0 titanium alloy.



a. b.

Figure 5. Surface morphology of the hydroxyapatite crystals grown on the surface of the VT1 titanium alloy obtained by optical microscopy after exposure to PIB: polished surface (a), etched surface (b).

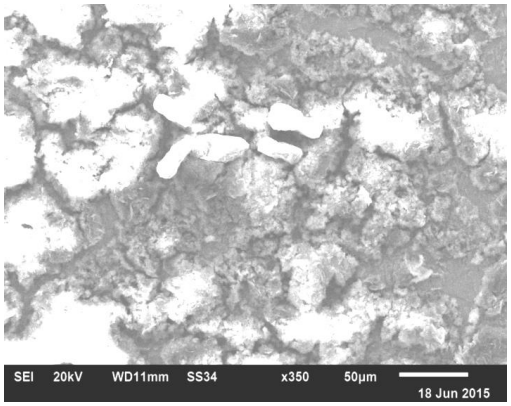


Figure 6. Surface morphology of the hydroxyapatite crystals grown on the polished surface of the VT1-0 titanium alloy after exposure to PIB.

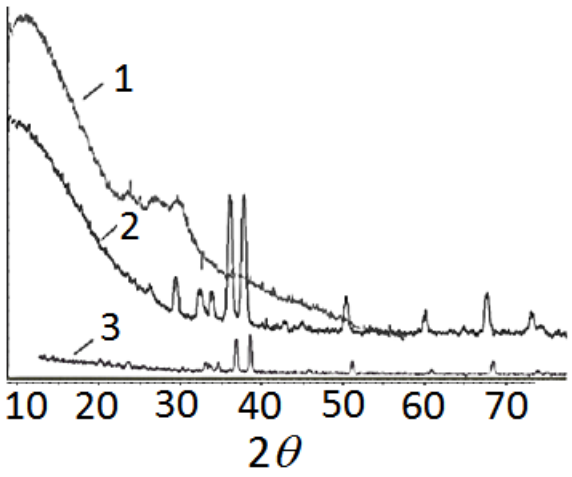


Figure 7. Diffraction pattern: GA-gelatin crystal sample (1); sample with HA crystals grown on the VT1-0 titanium alloy surface after irradiation (2); sample of the VT1-0 titanium alloy (3).

4. Conclusion

HAG-gelatin powders are synthesized from the SBF solution with gelatin content varying from 1 to 3 wt. %. It is established that all the samples synthesized in the medium of the model solution of the extracellular fluid at varying concentrations of gelatin are single-phase and represent hydroxyapatite.

Enhanced HAG-gelatin deposition on the titanium substrate surface is found to occur on etched samples. It is revealed that exposure of titanium substrates to PIB with j=100 A/cm^2 makes possible further growth of HA crystals and regeneration of the metal implant surface.

Acknowledgements

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