A Biocompatible Calcium-Phosphate Thin Coating Prepared by Magnetron Sputtering[1]

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Abstract – Calcium phosphates thin films are deposited by DC reactive and rf – magnetron spattering. Chemical and phase compositions, the mechanical and structural properties of thin films are investigated by the Rutherford Backscattering of α-particles and SEM techniques. The results show that the calcium phosphate thin films prepared by DC reactive – and rf-magnetron sputtering have the high packing density good adhesion and smooth surface. The coatings demonstrate satisfactory toxicological properties, have small dissolubility in bioactive liquids, and decrease the substrate solubility and extraction of alloying elements in external solution. Examination of tissue reaction in vivo shows that there is no inflammation and infectious development for all groups of observations. Probability of tissue lamina formation from column of bone marrow on such films is small.

1. Introduction

The problem of biocompatible coating formation on the materials of medical implants such as cobalt chromium alloys, bio-ceramics and polymers is very important. A coating has to be nontoxic, to suppress diffusion of metallic atoms and ions from implants into surrounding external tissues, to have great surface adhesion. It should not induce immune reactions and degrade while interacting with living tissues.

Nowadays there are two main investigation courses: 1) the bioactive coating: formation of thin calcium-phosphate films which combine bioactivity and mechanical strength; 2) the bio-inert coating: formation of thin calcium-phosphate films to improve the hemocompatibility of surface; strong, uniform, hyperfine, bio-inert coating producing on the extremely smooth surface of implant.

Calcium phosphates are the main components of bones and as coating, they promise optimal bone integration of an implants.

The object of this work is application of the magnetron sputtering process to the deposition of calcium-phosphate coating on the materials of medical implants. The results of complex investigation of microstructure, elemental composition, solubility and biological testing in vitro of Ca-P coatings prepared by DC and rf-magnetron sputtering deposition techniques upon metallic substrates are discussed.

2. Materials and methods

The coatings are deposited on the metals used in medicine: technical pure titanium, 316L stainless steel, and the titanium alloys Ti6Al4V. Sputtering has been made by magnetron both direct current and high frequency method.

Sputtering of calcium phosphate (Ca-P) coatings by direct current method is made by ion plasma installation for modification of surfaces and thin films deposition "Microcraft" [1]. The surface coating is made by sputtering of conductive cathodes in vacuum by plasma of abnormal discharge of a magnetron type (MSP process). Argon is used as the working gas.

In the direct current regime, a magnetron target is a cell structure titanium mandrel, in which there is a mixture of synthetic hydroxyapatite (the particle dispersion up to 78 nm) and zirconium oxide stabilized by yttrium oxide to provide the greater strength of ceramic. The target is baked in vacuum at 1100 °C.

In an alternative current regime, the Ca-P coatings are prepared by "Cathode 1M" installation with rf-magnetron sputtering. The frequency is 13.56 MHz, argon or mixture of argon and oxygen represents the working gas, the pressure in a vacuum chamber is (0.1–1.0) Pa. The target is made from synthetic hydroxyapatite with particle dispersion up to 78 nm.

In order to control the element composition of coatings produced by magnetron sputtering in both regimes, we use the Rutherford backscattering method. The samples are arranged on a calibrated ruler in vacuum chamber. While analyzing, we used the 1.7 MeV helium ion beam at the scattering angle 175° and the spectrometer energy resolution 11 keV. The coating element concentration profiles and their distribution are derived from the RBS spectra by a computer modeling, using the BS program.

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Adjustment at given parameters is made in an automatic regime. In order to improve the experiment accuracy, we use an inner monitor, i.e. the yield of scattering from substrate atoms.

We apply a Scanning Electron Microscope SEM 515 PHILIPS for studying the surface morphology.

3. Results and Discussions

Investigation of Ca-P coating morphology by Scanning Electron Microscopy technique shows that relief of the coating surface becomes more significant with increasing of the deposition time (fig. 1). Film growth occurs as a result of islands formation and subsequent grows of its size by coalescence.

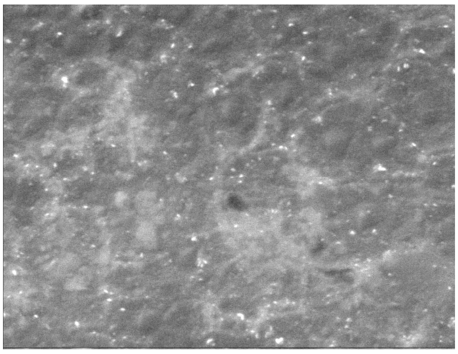

Fig. 1. The SEM image of Ca-P coating prepared by rf-magnetron sputtering on the titanium substrate. Time of deposition is 80 min. Magnification is 10000

The structure of Ca-P coating is uniform and dense without visible defects on the surface.

Fig. 2 shows a typical random energy spectrum of alpha particles scattered by a Ca-P coating deposited by a rf-magnetron method. It is obvious that calcium Ca, phosphorus P, and oxygen O are present.

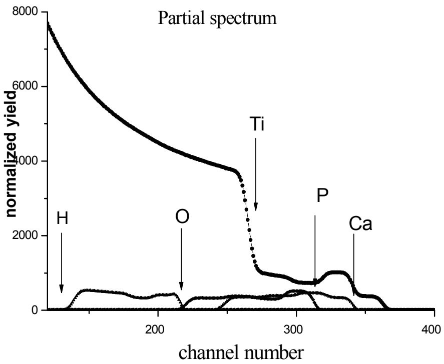

Fig. 2. The energy spectrum of alpha particles scattered by Ca-P rf-coating at an angle 170°

In accordance with RBS spectra, we have found the concentration profiles of the samples under investigation. Fig. 3 shows the concentration profile of Ca-P coatings prepared by rf-sputtering. The average elemental composition through the depth is Ca – 45.4±1.1 at%, P – 13.6±0.5 at%, and O – 41.1±0,7 at%, the depth concentration being practically constant.

While scanning films by an analyzing beam, in the back scattered spectra we observed sometimes the yield of titanium from the film surface. It confirms that the coatings of the thickness less than 200 nanometers are not continuous. The CCa/CP ratio depends on the sputtering regime and is in the range 1.7–4.0. The sputtering rate (according RBS method) is 0.5 micron per hour.

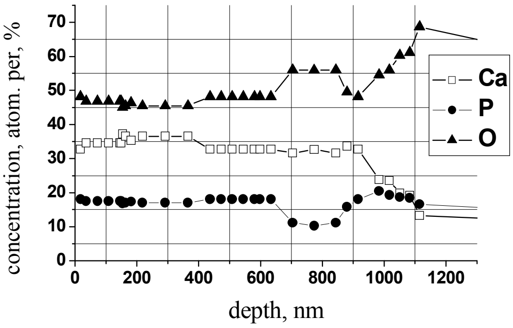

Fig. 3. The coating elements distribution obtained by RBS-analysis. rf-magnetron sputtering

The element distribution profile sputtered by MSP method as the function of the coating thickness is shown in Fig. 4. The depth element composition is almost uniform: O – 66.5±2,8 at%, Ti – 19.8±1,6 at%, P – 5.3±0,4 at%, Ca – 6±1 at%, Y – 2.3±0.4 at%. There is no accurate substrate – coating boundary, i.e. there is a diffuse layer, where the atoms of coating and substrate are mixed. Its thickness is about 60 nanometers. Besides the above-mentioned elements, the film contains also a small quantity of aluminum, copper, and carbon, which is due to the magnetron anode diffusion process during sputtering.

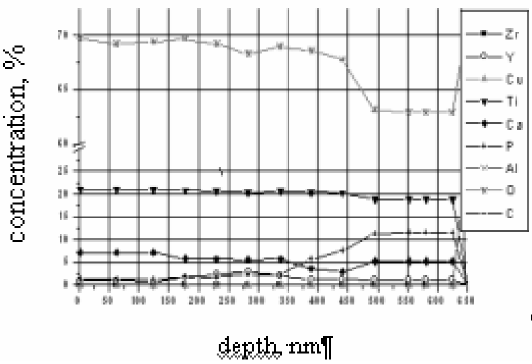

Fig. 4. The coating element distribution profile, sputtered in a magnetron direct current regime

An average ratio Ca/P=1 that is less than that for the bone tissues. It can be explained by the DC magnetron sputtering process [5]. According to [3], in the coatings produced by rf sputtering, the ratio Ca/P is 1.77–1.79. We confirm this quantity. The data got by MSP and rf methods are shown in Table 1.

The table shows that the rf sputtering method allows getting the coatings with the element composition (Ca, O, and P) close to that of the osseous tissues. A calcium amount gotten by the alternative current sputtering is about four times greater than that gotten by MSP method.

Table 1. The coating element composition produced by MSP and rf-magnetron sputtering

Element	Average concentration (at %)	
	MSP	rf-sputtering
Ca	6.0	26.2
P	5.3	5.81
O	66.5	67.4
Y	2.25	–
Zr	0.2	–
Ti	19.8	–

The Ca-P ratio affects the coating compatibility with a biological medium. In our experiments, the Ca-P ratio is about 1.0 for MSP method and about 4.0 for films produced by rf sputtering. The Ca-P coatings depending on different physics chemical parameters (thickness, crystallization degree, porosity, solubility, roughness, and the like) have different biodegradation rate [4]. The biodegradation of different Ca-P coatings is not clear and should be investigated.

Experiments on dissolution Ca-P coatings upon different metallic substrates have been made in a sterile 0.9 % sodium chloride solution in accordance with ISO 10993-5 (1992) recommendation. Samples (10x10 mm) are put in plastic test tubes with dissolvent (antibiotic gentamycin 30 mg/l) and undergo treatment in a thermostat at 37 °C during seven days (Table 2).

Table 2. Extracts of magnetron coatings on different substrates after seven days degradation in natrium chloride solution

Sample	pH	% of pH substrate	Ca++, mg/l	Ni+, mcr/l
Ni	7.18	–	–	740
Ni +Ca-P	7.24	101	2.01	280
TiNi	6.36	–	–	39
TiNi +Ca-P	7.08	111	2.4	32.6
Ti	6.45	–	–	–
Ti +Ca-P	7.01	109	2.9	–
TiAlV	6.6	–	–	–
TiAlV +Ca-P	7.25	110	3.59	–

The extract pH and concentration of bioactive (ionized) calcium has been controlled by amperometrical titration.

A sanitary chemical test (Table 2) shows that the thin Ca-P magnetron coatings almost do not change the solution composition. The pH quantity of extracts increases not greater than 9–11 % when the ionized calcium quantity increases 2–3 times. On the other hand, the thin Ca-P films can decrease solution of substrates and extraction of alloying elements. In particular, nickel (toxic, allergen, and carcinogen) extraction in solution decreases three times from the substrates with protecting coatings.

Biological tests in vitro have been carried out in accordance with prescription of ISO 10993-5. Cytotoxicity test was done with trypane blue. Testing in vitro demonstrates satisfactory toxicological properties of obtained composite (metal + Ca-P) implants. Bone marrow cells survivability are 89.56 % (at 90.49 % in the control) for Ca-P coating on titanium substratum and 97 % for stainless steel one.

4. Conclusions

1. HF magnetron sputtering method allows getting Ca-P coatings with elemental composition close to that of bone tissues.
2. The structure of deposited coating is uniform, dense, without any visible defects.
2. The Ca-P coatings practically does not dissolve in an isotonic sodium chloride solution.
3. The thin Ca-P films can reduce the solubility of substrates and extraction of alloying elements (for example nickel with high toxic potential).

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