PVD barrier coatings with antimicrobial function for medical implants

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Abstract. The technology of PVD coatings made of titanium and hafnium nitrides for implants was developed and properties of coatings were investigated. The coating as a barrier reduces the release of toxic vanadium ions from titanium alloys. The thickness of the coating is 2-5 microns with a characteristic structure size of 20-50 nm. The rate of migration of hafnium and titanium ions from the nitride coating into water is span of pico-femto mol/cm²h. The presence of cytocompatibility with human fibroblasts is shown. The coating is promising for combating microorganisms with high biofilm-forming activity.

1. Introduction
Metal alloy containing vanadium or molybdenum, nickel, cobalt, chromium can cause allergic reactions. The over coating as a barrier reduces the exit of ions from the implant into body tissue. The coating material must not be subjected to biological corrosion and be a source of toxic elements. The combined coating nitrides of titanium and hafnium are resistant to aggressive human environments and additionally inhibit the growth of pathogenic microflora [1].

2. Experimental
The calculation of the condensation rate of coatings (Hf+Ti) N on screws for osteosynthesis was carried out on a PVD tool with three electric arc evaporators at arc currents of 60-75 A in the geometric space of a cylinder rotating in the center [2]. Depending on the solid angle β from the axis of the ion flow, the condensation rate and the thickness of the coating of the track varies according to the cosine law. The rate of condensation of the coating on the solid angle section is determined by the formula:

\[ V = V_0 \cdot k' \]

\[ k' = \frac{R^4}{(R^2+h^2)^2} \cdot \frac{R^2 (R^2 - r^2 - r \cdot \cos \beta)}{(R^2 + r^2 - 2rr \cdot \cos \beta)^2} \]  

where \( V_0 \) - is the experimental velocity along the evaporator axis, \( k' \) - is the velocity coefficient when the flow deviates from the axis by a solid half-angle β.
The initial condensation rate $V_0$ is determined experimentally. It was in the range of 2.80 microns/hour to 2.88 microns/hour with a confidence factor is 0.9. The boundary conditions of the calculation are taken for two evaporators at $n=2.5$ rpm and the geometric configuration of the installation and $r=125$ mm. The calculation is carried out for $\beta = 0^\circ, 15^\circ, 30^\circ, 45^\circ$. Calculated that the rate of condensation of the coating by the simultaneous operation of the two evaporators, depending on the half opening angle of vapor plasma takes values $V_{0^\circ}=5.10$ microns/hour, $V_{15^\circ}=4.6$ microns/hour, $V_{30^\circ}=1.96$ microns/hour. The thickness of the coating per revolution is 34 nm, 27 nm, 13 nm, respectively. The rate of condensation of the coating (thickness) falls by 2 times at angles of spread of more than 30°, which is unacceptable due to the reduction of the coating thickness. Therefore, the implants should be placed with a deviation from the axis of the evaporator no more than 200 mm.

The composition and structure of the condensate layers were studied at the Auriga CrossBeam station of Carl Zeiss using the INCA energy dispersion spectrometer of Oxford Instruments using ion etching. The layered structure of the coating is shown in figure 1.

![Figure 1. Element distribution layers.](image)

The presence of hafnium and titanium oxides in the molar ratio of 1:4 was found in the composition of the outer layer at depths of several atoms. Atmospheric oxygen and water oxidize the outer layers of nitrides on the surface in the form of active nanostructures to oxides due to high enthalpy values of their formation in 265 and 225 kcal/mol and high chemical activity. The integral composition of the chemical elements of the coating at thicknesses up to 10 microns showed the ratio of hafnium and titanium in equal mass fractions with variations of ±20%. The molar fraction of titanium is 3.5 times greater than hafnium. Crystals of the combined coating have a length of coating thickness and a diameter of 20-50 nm. The growth of columnar crystals is not interrupted by the transition from one evaporator of the metal vapor-plasma phase to another. In the electron spectroscopic image, a thin interface between TiN and HfN is visible, which is captured only by the spectrometer. There is no phase boundary, which is typical for nanostructures.

The rate of ion migration was estimated experimentally through the concentration of the corresponding element in the aqueous extract from a known surface over time. The concentration was determined according to the recommendations of ISO 10993-12-2011. Determination of trace concentrations of chemical elements in the solution was performed by x-ray fluorescence spectroscopy S2 PICOFOX (BRUKER) and mass spectrograph brand NexION 300D (PerkinElmer) with a sensitivity of 0.1-1.0 ppt. Before measurements spectrometers were calibrated on the required elements Hf, Ti, V, as well as on the elements-markers-Se, and later Ga. Quartz reflector (cuvette) and water for research were tested in a control experiment.

### 3. Results of experiments and discussion

Analysis of the results with high fidelity of evidence (dispersion 5-7%) shows the presence of detectable concentrations of hafnium and titanium in water. The reliability of the determination of vanadium V is low, however, the ultra-low concentration of the element can indirectly state the presence of protective functions of the coating and prevent the migration of toxic vanadium ions from
the vanadium-doped titanium alloy into the water. The rate of migration of ions from the coating was determined at exposure in the liquid up to 720 hours. Measurements of the concentrations of the elements of interest showed that their concentrations ranged from 4 ng / liter to 24 ng / liter, with titanium and hafnium in the Protocol determined by isotopes. The concentration of titanium in isotonic sodium chloride solution is 5 times higher than in water, which does not contradict the theory, and hafnium has 2 times less. The rate of corrosion of titanium from the coating into the water is in the range from $2.8 \times 10^{-13}$ to $4.0 \times 10^{-15}$, and hafnium from $3.5 \times 10^{-14}$ to $5.6 \times 10^{-16}$ mol/cm$^2$ hour. This corresponds to a weight loss screw for osteosynthesis of $10^{-7}$ to $10^{-9}$ grams in one year. The rate of hafnium corrosion decreases by two orders of magnitude with increasing contact time with water from a day to a month.

Presumably, hafnium ions in water are surrounded by water molecules and dissociated in one reaction. The acid residues of (HfO)$^-$, (TiO)$^-$ show inhibition of the growth of pathogenic microflora, including microbial biofilms under implants.

Research on cytotoxicity (toxicity to living cell structures) was carried out on transplanted cultures of animal and human origin. The growth of passage culture such as NGUK-1, SPEV, TR on a surface coated with (Hf + Ti)N showed a value of 1.4 to 1.9 of the proliferation index. Passage cultures accreted to the surface with a titanium-hafnium nitride coating, as well as to the glass surface. Studies on human transplanted fibroblasts showed with high reliability (0.95) the absence of cytotoxic effect of the coating on living cell cultures. Studies on human transplanted fibroblasts showed with high reliability (0.95) the absence of cytotoxic effect of the coating on living cell cultures. The cell viability pool was 84.2%, the proliferative index was 2.02, the cell population doubling time was 95 hours for the coating, compared to 82.7 hours for the glass surface.

4. Conclusion

1) The rate of corrosion (migration of ions) of hafnium and titanium from the nitride coating into water is extremely small and is approximately pico-femtomol / cm$^2$ h, which amounts to the loss of several nanograms per year from the implant

3) The migration rate for 720 hours hafnium ions from nitride coatings into water falls by about two orders of magnitude and further migration of ions slows down;

4) The protective coating based on hafnium nitrides is cytocompatible with human fibroblast cells and does not possess cytotoxicity;

4) Coating based on hafnium and titanium nitrides is promising as a biocompatible coating for implants with barrier and antimicrobial effect in the fight against microorganisms with high biofilm-forming activity [3].

References

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