NEW METHODS FOR MEASURING THE PROPERTIES OF ANTIBIOGENIC COATINGS OF MEDICAL TITANIUM IMPLANTS FOR TRAUMATOLOGY AND ORTHOPEDICS

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Abstract: The work is a part of researches of the technical characteristics of 20 types of medical titanium implants for traumatology and orthopedics with antibiogenic coating of titanium and hafnium nitrides in accordance with technical conditions of the manufacturer of the implants – JSC “Medmash”, Russia. Based on a titanium alloy the implant with antibiogenic coating is a product coated with titanium and hafnium nitride by high-frequency magnetron sputtering.

In the present article, the structure, phase composition, distribution of elements on the surface and thickness (Ti-Hf)N-coatings with different hafnium content (Ti:Hf ratio) were investigated. The studies were carried out on model samples in the form of plates of titanium alloy VT6, which were coated with titanium and hafnium nitride by magnetron sputtering. Also, changes in the thickness of the hardness and modulus of elasticity of the coatings were measured by the method of instrumental indentation. The maximum values of hardness (~35 GPa) and modulus of elasticity (~500 GPa) were obtained from coatings of composition (Ti0.8Hf0.15)N and (Ti0.8Hf0.2)N. The coatings with these compositions have the most uniform Hf thickness distribution.

KEYWORDS: (Ti-Hf)N- COATING, STRUCTURAL PROPERTIES, MECHANICAL PROPERTIES

1. Introduction

The development of new nanostructured coatings with high hardness values (> 40 GPa), elastic modulus and high thermal stability (> 1200 °C), as well as long-term stability, is one of the urgent tasks of modern materials science. Such coatings have a wide range of applications, among which protection of products with different functional purposes (increased crack resistance, wear resistance of the cutting tool, its hardness; improvement of thermal, chemical and radiation resistance of products) [1]. The practical use of superhard nanostructured coatings poses the problem of expanding the range of protective functions, as well as their combination in one coating material.

Research of the physical causes of high physical and mechanical properties of nanostructured materials, including coatings, has been intensively carried out in recent decades. The basis of these studies is the study of the composition and structural features of coatings, which is associated with the existence of dependence for nanomaterials on the “composition-structure-dispersion-property” [2].

A special position is occupied by coatings based on titanium nitride (TiN). A large amount of work is occupied by the study of the properties of superhard nanostructured coatings of a new type based on (Ti-Hf-Si)N and (Ti-Hf)N, on silicon and steel substrates [3-5]. With the help of modern physical methods of analysis and nanoindentation, the elemental composition, phase composition and morphology of these films were studied depending on the parameters of their production. The dependences of their hardness on the grain size, on the phase composition of the films are established.

An important area of application of protective coatings based on (Ti-Hf)N – a bactericidal coating of medical products made of titanium. Hafnium nitride contained in these coatings gives them bactericidal, bacteriostatic properties and increases the microhardness of the surface. Currently, there are works in which coatings with different mass fraction of elements are used: w(Ti) 17-24%, w(Hf) 70-80% and w(N) 3-6%. The use of such a coating for titanium implants that experience long-term contact with tissues of a living organism provides increased hardness and has bacteriostatic properties, preventing the proliferation of pathogens near the implant [6-8].

The nomenclature of implants manufactured by JSC “Medmash” includes more than 20 items. These are screws for osteosynthesis, straight and figured plates, tubular plates, rods for various bones, screws for various purposes, as well as dynamic implant designs. Implants are made of titanium alloy and, as a rule, have a protective coating, which gives the product a high hardness, strength and durability. An implant based on a titanium alloy with an antibiotic coating represents an product coated with titanium and hafnium nitride by high-frequency magnetron sputtering.

This article presents the results of studies of the chemical composition, phase composition, structure and mechanical characteristics (hardness, elastic modulus) of (Ti-Hf)N-coatings with different hafnium content (Ti:Hf ratio). The thickness distribution of the coating chemical composition and mechanical characteristics were evaluated.

2. Samples and methods

The samples were plates of titanium alloy VT6 with thickness of 3.0 mm (chemical composition according to GOST 19807), which were coated with titanium and hafnium nitride by magnetron sputtering. Antibiotic coatings of titanium and hafnium nitrides were produced in "Biomedical technologies" JSC at the installation “Energomcomplex” of high-frequency magnetron deposition of coatings. For the manufacture of the cathode for coating the product by magnetron method used titanium-hafnium alloy. To determine the dependence of the coating characteristics on the Hf content, samples of coatings with a thickness of ~3.0 µm of 4 nominal compositions were prepared and studied: (Ti0.7Hf0.3)N, (Ti0.6Hf0.4)N, (Ti0.5Hf0.5)N, and (Ti0.3Hf0.7)N.

Surface morphology and chemical composition of coatings (Ti-Hf)N were investigated by scanning electron microscope (SEM) JEM 7600F with adaptors for analysis of characteristic energy-dispersion (EDS) and wave dispersion (WDS) spectra of chemical elements. EDS and WDS spectra readings were taken from the surface of the coatings. In determining the chemical composition the spectra readings were taken from the area of three SEM images (frames) of the surface of each sample, and the data of EDS and WDS were averaged separately. EDS measurements used standards originally laid down in the SEM, and in the case of WDS measurements used external standards: Hf-(La Hf_15kV), V-(Ka V_15kV), Ti-(Ka Ti_15kV), O-(Ka Al2O3_15kV), N-(Ka BN_15kV) and C-(Ka C_15kV).

Also, with the help of EDS the dependence of the chemical composition of the thickness of the coating was analyzed. To study the distribution of the composition in thickness on the samples in the form of plates 10×10×3.0 mm, cuts were created in thickness with a depth of ~2.9 mm and the sample was broken into these cuts. Electron microscopic measurement, as the thickness of the coating, and the composition distribution throughout the thickness of the coating was carried out on these splits. X-ray diffraction patterns of the samples were obtained on the EMPYREAN diffractometer (PANalytical), in vertical geometry 0-0, radiation CuKα1+2. XRD patterns were taken in continuous
These coatings are presented. Hafnium distribution maps by area of images (b), spectral patterns presented. Nitrogen distribution maps over the area of the images are the coating sections of samples (Ti-Hf)N, and titanium and distances from the coating surface. In Fig. 2 the SEM images of "injections" (indentation tests) was 2 µm.

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Figure 1. SEM images of the coating surface (Ti, Hf) N on the alloy of titanium BT-6.
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Table 1. EDS (regular font) and WDS (italics) analysis of all elements is performed (normalized). All results in atomic%.

<table>
<thead>
<tr>
<th>Coating</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>Na</th>
<th>Al</th>
<th>Si</th>
<th>Ti</th>
<th>V</th>
<th>Mn</th>
<th>Rb</th>
<th>Hf</th>
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<tr>
<td>Ti₆₅Hf₃₅</td>
<td>0.01</td>
<td>51.31</td>
<td>58.45</td>
<td>0.34</td>
<td>0.05</td>
<td>41.66</td>
<td>36.86</td>
<td>3.03</td>
<td>0.12</td>
<td>0.20</td>
<td>5.68</td>
<td>7.33</td>
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<tr>
<td>Ti₆₅Hf₃₅</td>
<td>0.75</td>
<td>48.39</td>
<td>57.55</td>
<td>1.38</td>
<td>0.05</td>
<td>40.46</td>
<td>34.92</td>
<td>2.29</td>
<td>0.05</td>
<td>0.52</td>
<td>8.55</td>
<td>4.73</td>
</tr>
<tr>
<td>Ti₆₅Hf₃₅</td>
<td>0.63</td>
<td>49.47</td>
<td>57.42</td>
<td>0.44</td>
<td>0.05</td>
<td>38.03</td>
<td>33.55</td>
<td>0.30</td>
<td>0.24</td>
<td>1.24</td>
<td>10.57</td>
<td>3.60</td>
</tr>
<tr>
<td>Ti₆₅Hf₃₅</td>
<td>0.47</td>
<td>45.42</td>
<td>56.23</td>
<td>0.58</td>
<td>0.20</td>
<td>36.99</td>
<td>30.73</td>
<td>0.39</td>
<td>0.43</td>
<td>1.56</td>
<td>10.70</td>
<td>2.33</td>
</tr>
</tbody>
</table>

3. Results and discussion

3.1. Chemical composition and distribution of elements

SEM images of the surface of four samples (Ti-Hf)N coating on titanium alloy VT-6 and the chemical composition of the surface are shown in Fig. 1. With increasing Hf content, the coating surface becomes more defective with the formation of extended and more pronounced boundaries of the surface areas. The fine-grained structure of the coatings indicates a sufficiently high deposition rate.

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Table 1. Chemical composition, at.%
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<table>
<thead>
<tr>
<th>Coating</th>
<th>Chemical composition, at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti₆₅Hf₃₅</td>
<td>C 51.31, N 58.45, O 0.34</td>
</tr>
<tr>
<td>Ti₆₅Hf₃₅</td>
<td>C 48.39, N 57.55, O 1.38</td>
</tr>
<tr>
<td>Ti₆₅Hf₃₅</td>
<td>C 49.47, N 57.42, O 0.44</td>
</tr>
<tr>
<td>Ti₆₅Hf₃₅</td>
<td>C 45.42, N 56.23, O 0.58</td>
</tr>
</tbody>
</table>

3.2. SEM images and chemical analysis for coating thickness

The distribution of the basic elements (Ti, Hf, N) was determined both over the entire area of the SEM image (mapping) and along lines and in points lying at different distances from the coating surface. In Fig. 2 the SEM images of the coating sections of samples (Ti-Hf)N, and titanium and nitrogen distribution maps over the area of the images are presented.

In Fig. 3 the SEM images with EDS lines and points (a), hafnium distribution maps by area of images (b), spectral patterns along line 1 for Ti₆₅Hf₃₅ and at point 5 for Ti₆₅Hf₃₅ (c) and distribution of the basic elements (N, Ti, Hf) in the thickness of these coatings are presented.

The same data, with the exception of the spectral patterns, for coatings Ti₆₅Hf₃₅ and Ti₆₅Hf₃₅ are shown in Fig. 4.

Chemical composition measurements were carried out on two SEM images at different cross-section locations and these data were practically identical.

It can be concluded that in all coatings the concentrations of the basic elements are uniformly distributed over the thickness of the coating, except for the point lying near the surface. At this point, the concentration of Hf and, to a greater extent, N, is reduced.
Such a pattern was noted in [7], where, even with the thickness (Ti-Hf)N of the coating in 1-1.5 µm, the subsurface layer was depleted by Hf and N. It is most likely that this phenomenon is due to the formation of a thin film of aluminum carbide in the near-surface layer [10], or other metal present in the layer.

Figure 2. SEM images of sample splits (Ti-Hf)N (a), titanium (b) and nitrogen (c) distribution maps over the area of the images.

Figure 3. SEM images with EDS lines and points (a), hafnium distribution maps by area of images (b), spectral patterns along line 1 for Ti$_{0.7}$Hf$_{0.3}$ and at point 5 for Ti$_{0.9}$Hf$_{0.1}$ (c) and distribution of the basic elements (N, Ti, Hf) in the thickness of coatings (d).

Figure 4. SEM images with EDS points (a), map of hafnium distribution by area of images (b) and distribution of the main elements (N, Ti, Hf) for the thickness of coatings along points for Ti$_{0.8}$Hf$_{0.2}$ and Ti$_{0.85}$Hf$_{0.15}$ coatings (c).
3.3. Structural studies

X-ray diffraction studies of the phase composition of the coatings showed the presence of only one phase: titanium nitride with HCC lattice of NaCl, B1Fm3m type [10]. On all XRD patterns shown in Fig.3 there are diffraction peaks (111), (200), (220) and (222). The intensity of the peaks indicates that it is a single-phase polycrystalline titanium nitride. Table 1 shows the dependence of the lattice parameters in the (Ti,Hf)N coatings on the concentration of hafnium.

![Figure 3. XRD patterns of four samples (Ti-Hf)N coatings](image)

As it is known [10], TiN (structural type NaCl) crystallizes in the space group Fm3m with the parameters of the unit cell: a=0.422-0.426 nm. The estimation of crystal sizes by coherent scattering region showed that coatings with a high content of Hf have smaller grain size.

There is a monotonic increase in the crystal lattice parameter of titanium-hafnium nitride with an increase in the Hf content. This can be explained as follows. Titanium nitride coatings are not ideally stoichiometric due to the wide area of homogeneity of the TiN. Therefore, its properties are highly dependent on the amount of nitrogen in the nitride. The decrease in the nitrogen concentration, which is established according to the SEM, leads to the formation of a defective structure due to the lack of nitrogen atoms in the metal lattice. In addition, an increase in the lattice parameter may indicate a high level of internal stresses.

3.4. Raman spectroscopy

In Fig. 4, the Raman spectra obtained at a wavelength of exciting radiation of 532 nm are presented.

![Figure 4. Raman spectra of four samples (Ti-Hf)N coatings](image)

Pure TiN has a structure of NaCl type, and in the Raman spectrum the bands associated with the density of states of acoustic modes (225 cm\(^{-1}\) (TA) and 310 cm\(^{-1}\) (LA)) and optical mode in the region of 540 cm\(^{-1}\) are manifested. In the Raman spectra of the studied samples there are bands in the region of 220 cm\(^{-1}\) (shoulder), 272 cm\(^{-1}\), 540 cm\(^{-1}\), 805 cm\(^{-1}\) and 1083 cm\(^{-1}\). The bands in the area of 220 cm\(^{-1}\), 272 cm\(^{-1}\) and 540 cm\(^{-1}\) belong to phase (Ti-Hf)N with NaCl type structure (similar to pure TiN).

The presence of bands in the region of more than 700 cm\(^{-1}\) may be associated with the appearance of chains of polyhedra \([\text{TiN}_x]\). Polyhedra \([\text{TiN}_1]\) correspond to the band with a maximum in the region of 700 cm\(^{-1}\), and \([\text{TiN}_2]\) - in the region of 840 cm\(^{-1}\).

The introduction of Hf into the structure leads to the displacement of bands towards large wave numbers. Thus, the band in the region of 272 cm\(^{-1}\) in the sample \((\text{Ti}_{0.7}\text{Hf}_{0.3})\text{N}\) shifts to 295 cm\(^{-1}\) in the sample \((\text{Ti}_{0.8}\text{Hf}_{0.2})\text{N}\). The shift towards large wave numbers may be related to the stresses arising in the titanium nitride–hafnium coating.

4. Mechanical properties

In Fig.5 a photo of the measurement area of one of the samples is shown.

![Figure 5. A photograph of the area in which the indentation was made.](image)

Data of the dependence of the hardness on the profile coordinates are shown in Fig.6. The Fig.7 shows the change in the hardness of the coating thickness. The hardness drops towards the substrate at a distance of less than 1 µm to the substrate boundary (due to the effect of the substrate properties).

![Figure 6. Dependence of the hardness of the samples on the coordinate Y. The origin was on the substrate, the point (0; 125) was on the coating. Figures in the legend to the graph indicate the numbers of the samples (1- \((\text{Ti}_{0.7}\text{Hf}_{0.3})\text{N}\), 2- \((\text{Ti}_{0.8}\text{Hf}_{0.2})\text{N}\), 3- \((\text{Ti}_{0.9}\text{Hf}_{0.1})\text{N}\), 4- \((\text{Ti}_{0.8}\text{Hf}_{0.2})\text{N}\)).](image)

The average results of measurements of hardness \((H_5\) and \(H_C\)) and elastic modulus \((E_S\) and \(E_C\)) for the regions of the substrate (S) and coating (C) are given in the Table. 2.
The values of hardness and elastic modulus of the coating, within the error, are the same, do not depend on the content of Hf in the coating at the studied relations Ti:Hf and correspond to the hardness values known from the literature data.

### 5. Conclusion

The results of the study of the dependence of the composition, structure and mechanical characteristics (hardness, elastic modulus) on the content of Hf coatings (Ti-Hf)N on a substrate made of titanium VT6 were presented. The distribution of the chemical composition in the thickness of the coatings was studied. For the first time the hardness distribution over the thickness of coatings with different ratio Ti:Hf was studied. The heterogeneity of the hardness distribution over the thickness of the coating with the inhomogeneity of the distribution of Ti and Hf in the coating was established. The maximum values of hardness (~35 GPa) and elastic modulus (~500 GPa) were obtained from coatings of composition (Ti\(_{0.85}\)Hf\(_{0.15}\))N and (Ti\(_{0.8}\)Hf\(_{0.2}\))N. (in weight ratio (Ti\(_{40.7}\)Hf\(_{26.8}\)) and (Ti\(_{38.3}\)Hf\(_{35.7}\)). The coatings of these compositions were characterized by the most uniform distribution of Ti and Hf in thickness.

### 6. Acknowledgments

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### 7. References


