Characteristics and properties of nanolayer hafnium based PVD coatings

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Abstract. The paper presents an experimental study of the characteristics of a multilayer coating made of titanium and hafnium nitrides. The thickness of layers formed by the ion-plasma coating method was calculated. It was found that the biologically active coating based on titanium nitride and hafnium has a layered structure. The calculated layer thickness is in the range from 6 to 10 nm, the determined thickness is in the range from 10 to 20 nm. The topography of the coating surface contains intergranular boundaries that are reproduced as empty slits with a size of less than 5 nm. The transverse dimensions of the crystals can be estimated at 5-30 nm.

1. Introduction
Hafnium nitride, as a PVD coating and being an analog of zirconium and titanium nitrides, has similar characteristics in hardness, adhesion, strength, and structure. The structure of the electron shell and the physical constants of metal hafnium contribute to an increased value of the enthalpy of formation of hafnium compounds, but it also complicates the processes of metal sputtering in an electric arc discharge. Due to their high hardness, titanium and zirconium nitrides are used as a thin-film coating to increase the durability of metal-cutting tools. There is a small amount of research on the practical use of hafnium nitride in combination with titanium nitrides in medicine [1].

The small number of studies is explained by several reasons. Initially – this is the absence of ore deposits, the equivalence of chemical properties with analogues in the group and the high cost of the metal. Secondarily, these are the high melting temperatures of the metal and the extremely high evaporation temperature of 5200 K. This affects the instability of the electric arc in a vacuum at the hafnium cathode.

2. Results and Discussion
Refractoriness increases droplet formation during evaporation in the cathode spots. The reduction of droplet formation can be achieved by lowering the arc discharge current, which leads to low stability of the discharge at the hafnium cathode in industrial electric arc evaporators of ion-plasma equipment. High stability of the electric arc at the end of the cathode assembly for titanium, niobium and copper is achieved at currents of 50-60 A in the absence of a focusing current and at a current of 0.8 A stabilizing coil. A stable discharge on hafnium under the same conditions is not achieved.

Evaporation of hafnium from a combined titanium cathode with hafnium inserts allowed the evaporation of the refractory metal at stable combustion currents of 50-60 A. The coating contained
hafnium compounds in an amount of no more than 10% by weight. This practically did not affect the characteristics of the nitride coating. At the same time, the characteristics of the mixed coating were comparable with the results of other studies [2]. The scheme of assisting (accompanying) the arc discharge with ions of inert gas [3] allows to increase the stability of the operation of electric arc evaporators. The authors consider practically realizable the replacement of gas ions with metal ions from a number of stably burning ones. This requires an additional electric arc evaporator or the use of an ion purification evaporator. Additional initiation of the hafnium arc discharge with a higher voltage of 600 V and assisting by titanium plasma allowed to organize a stable arc burning at the Hf cathode at currents of 70-80 A under conditions of nitrogen pressure 0.1-0.2 Pa. The instability of the arc discharge at the hafnium cathode causes the intensive formation of microarc discharges on the surface of the coating. The developed technical measures, including the modulation of the bias voltage with an amplitude of up to 1.5 kV, with duration from 1 µs to 500 µs, a duty cycle of 10-500 Hz and a current of up to 2 A, made it possible to obtain high-quality coatings. At the same time, the surface of the products was intensively protected from the formation of micro-arc discharges on them. Condensation of PVD (CIB) coatings based on a mixture of nitrides can be carried out only when the substrate rotates around its axis in the chamber. The absence of such rotation leads to the deposition of a coating of different thickness along the axis of the electric arc evaporator and the limitation of the coating area, as shown in Figure 1 (a).

![Figure 1](image.png)

Figure 1. a) Upper and lower bounds of the interval of relative thickness V; b) The diameter of the coating pad H, depending on the value of the solid angle β of the deviation of the plasma flow of the evaporator from the axis of the evaporator in the absence of movement of the substrate

To obtain a consistent growth of columnar crystals of the protective coating, it is necessary to correctly calculate the condensation modes of the multilayer coating from the vapor-plasma phase under the conditions of rotation of the product in front of the evaporators. At the same time, at coating growth rates of more than 30 Å/min, germs are formed and their complete coalescence takes place, namely, the contact, fusion and displacement of the intergranular boundary of the particles. It would be wrong to think that increasing the ion energy during bombardment increases the adhesive strength of the sublayer. Loosening the surface and saturating it with metal ions can negatively affect the adhesive strength of the coating. The boundary layer forms an adhesive interaction due to intermolecular and chemical bonds. The boundary layer determines not only the amount of adhesive interaction, but also the type of separation – cohesive or adhesive. Fractal structures, for example, have little cohesive strength.

An experimental layer-by-layer deposition of a coating made of titanium and hafnium nitrides with the formation of a multilayer combined coating made of nanoscale layers was carried out. The calculated conditions of this process are shown in Table 1.

The linear calculated deposition rate of the titanium nitride coating \( V_0 \) was from 4.44 microns/hour to 4.95 microns/hour with a confidence probability of 0.9 at the arc evaporator current of 65 A. The growth rate of the hafnium nitride coating at the arc evaporator current of 75 A is in the range from 0.72 microns/hour to 0.82 microns/hour with a confidence probability of 0.9, which is five times lower than the growth rate of titanium nitride.
Table 1. Coating condensation modes.

| Chemical compound | Density, g/cm² | Arc current, A | Offset voltage, V | Nitrogen pressure, Pa | Distance to the cathode, mm |
|-------------------|----------------|----------------|------------------|----------------------|----------------------------|
| Titanium nitride  | 5.43           | 65             | 200              | 0.2                  | 600                        |
| Hafnium nitride   | 13.84          | 75             | 200              | 0.2                  | 600                        |

The growth of the coatings was measured under the same conditions in the stationary state of the sample, which was located opposite the cathode. The experimentally determined value of the condensation rate of titanium nitride is close to the values given in authoritative information sources and is, according to the researchers, 1.65 nm/s.

The geometric growth rate $V$ of the coating depends determinatively on the distance $r$ from the center of the vacuum chamber to the cathode and the angle $\beta$ of the deviation of the growth point of the coating from the axis of the arc evaporator. It is expressed by the dependence given in the sources.

From the analysis of the calculated data, it follows that when the angle of deviation from the axis of the evaporator is 15–20 degrees, the growth rate of the coating slows down twice. The vertical dimensions of the coating workpiece should not exceed 500–550 mm. Otherwise, the thickness of the coatings at the ends will be less than half the thickness of the central zone, and when the solid angle of plasma sputtering is 45 degrees, it will be close to zero.

The rotation of the workpiece with a frequency $n$, with a radius of rotation $r$ and the presence of three evaporators significantly complicates the calculation of the coating thickness [4]. Increasing the speed of the product leads to a decrease in the thickness of the layers, an increase in their number and the preservation of the overall thickness of the coating at the same time. The reverse action, with a decrease in the speed of rotation to 0 rpm, results in a coating on the product only in areas that are opposed to the evaporators.

The characteristics of the multilayer coating obtained by this technology are shown in Table 2.

Table 2. Characteristics of the Hf-Ti-N multilayer coating.

| Compound | Porosity, % | Hardness, GPa | Roughness, Ra, mkm | Phase | Layer thickness, nm  |
|----------|-------------|---------------|-------------------|-------|---------------------|
| TiN      | 2 – 3       | 3.2 – 14.5    | 0.05              | TiN₂, TiN | 2400 6 – 12       |
| HfN      | 3 – 5       | 4.8 – 7.6     | 0.2               | HfN₂, HfN | 2000 4 – 8        |
| (Ti+Hf)N | 3 – 4       | 4.8 – 12.0    | 0.1               | HfTiN, HfTiN₂ | 4400 10 – 20 |

With the nanoscale thickness of the coating layers and with the higher density of hafnium nitride, the mass ratio of titanium and hafnium should approach equal parts in the coating. Such a test for the convergence of the results of calculations and studies was carried out on Bruker's Tornado and Picofox X–ray fluorescence spectrosopes. The measurements confirmed an equal mass ratio of metals in the coating with variations of ±10%.

The layered structure of the coating with a layer thickness of 6-10 nm is clearly visible on spectrosopes due to the significant difference in the mass of the chemical elements titanium and hafnium. Figure 2 shows a cross-section of a multilayer titan-hafnium nitride coating using a high-resolution spectrum analyser. The cross-section is carried out by an ion beam flow. The layers with titanium and the layers with hafnium are clearly visible. In the adhesive sublayer and the centre of the cut of the coating, a zone with the absence of hafnium is visible, that is due to the coating technology and the formation of the adhesive layer.
Figure 2. Cross-section of the crystals coating with the layered structure of nitrides.

The thicknesses of the layers of 10-20 nm and the upper graphene layer are determined. Charges flow down it to the ground, preventing the areas from being illuminated. At the boundaries of the layers of titanium and hafnium nitrides during their joint condensation, a new phase of the compounds, defined as TiHfN₂, was revealed. Its formation can be interpreted as a phase of hafnium substitution in the Hf₂N₂ structure by Ti. Reflections with an index of 111 have the maximum intensity in the nitride phases, which confirms the predominant composition of the crystals and their growth in the direction perpendicular to the substrate. The result of this growth is the presence of columnar crystals in the coating.

Conclusions
1) The stability of the discharge increases, when an electric arc discharge of hafnium is assisted in a vacuum with metallic titanium ions. It also reduces the current of a stable arc discharge of hafnium to 70 A in nitrogen at a pressure of 0.2 Pa.
2) The titan–hafnium nitride coating, which has biologically active properties, has a layered structure with an estimated thickness of alternating layers of titanium nitride and hafnium nitride of 6-10 nm and a determined thickness of 10-20 nm.

References
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