Confidence of nano-measurements of Hf-Ti-N multilayer PVD condensates from the plasma phase

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Abstract. The microhardness and thickness of PVD coating layers made of titanium and hafnium nitrides were measured experimentally. The standards of TC 441 were analyzed. The sequence (protocol) of the analysis of nano-measurements and obtaining reliable measurement results was given. To obtain a quantitative value of the reliability of measurements for superhard nanocoatings is proposed to use for educational purposes the calculation of the confidence interval using the Student criterion.

1. Formation of nitride coating and its evaluation

The coating was condensed from the vapor-plasma phase on a device with three electric arc evaporators in a nitrogen atmosphere with a pressure of 0.2 Pa. Two evaporators with magnetic stabilization of the arc produced a phase of metallic hafnium, and one cathode evaporated titanium.

The discharge current of the evaporators was 60-75 A. A base was placed in the center of the chamber, which rotated and a reference voltage of 200 V was applied to it. The rotation frequency of the base was 2.5 min⁻¹. The coating was condensed in layers. The layout of electric arc evaporators is shown in Figure 1.

![Figure 1](image_url)

Description: 1 - vacuum chamber, 2 - rotating cylindrical sample holder, 3, 4 - arc evaporators.
The formation of the nitride layer occurs when the sample passes through the spray zone of the arc evaporator. Two layers of hafnium nitride and a layer of titanium nitride are condensed sequentially. The density of hafnium is greater than the density of titanium. Therefore, the thickness of the two layers of hafnium nitride is approximately equal to the thickness of the titanium nitride layer. As the rotation speed of the product increases, the thickness of the layers decreases, and their number increases. At the same time, the total thickness of the coating formed during the same time remains the same. The condensation conditions were described in detail in the materials of previous studies [1].

The formation of such a multilayer coating structure contributes to the overlap of the intergranular boundaries of steel. This prevents the formation of through pores even in a thin coating. The coating surface contains a phase of microdrops.

Figure 2 shows a section of the entire thickness of the coating with layers of nitrides. It was recorded by a high-resolution spectroscope on the Auriga station platform.

Multiple overlapping of the substrate phase separation zones by nanoscale layers leads to the formation of bridges, their coalescence and disruption of the ordered crystalline columnar structure of the coating. Another type of nanostructure is formed. The formation of a new phase of HfTiN₂ was revealed. It is not marked in Bruker catalogs.

![Figure 2](image_url)

**Figure 2.** Section of a multilayer coating with a total thickness of 2500 nm.

The results of measuring the main characteristics of the coating and layers are shown in Table 1. Microhardness was measured on a PMT-3 microhardness meter in manual mode at loads of 20 and 50 grs.

| Compound | Layer thickness, nm | Hardness, GPa | Roughness parameter, Ra, microns | Phase | Number of layers | Confidence |
|----------|---------------------|---------------|---------------------------------|-------|-----------------|------------|
| TiN      | 2400                | 3.2-14.5      | 0.05                            | TiN₂, TiN | 1               | 0.8        |
| HfN      | 2000                | 4.8-7.6       | 0.2                             | HfN₂, HfN | 1               | 0.8        |
| (Ti+Hf)N | 2500                | 4.8-12.0      | 0.1                             | HfTiN₁, HfTiN₂ | 70 - 90 | 0.8        |

The thickness of the layers of titanium and hafnium nitrides was determined by calculation using the growth rate of the coating on a fixed substrate. The actual thickness of the layers was measured experimentally by the coating section based on the total thickness and the number of turns of the substrate during coating application. The confidence probability was set.
2. A reliability of the measurement results of the characteristics of nanoobjects

The Technical Committee of TC 441 of the State Standard “NANOTECHNOLOGY” has practically completed regulatory documentation in the field of nanotechnology over the past 10 years. The standards carry out technical regulation according to methods, measuring systems and requirements for nanodispersions, fibers, coatings and composites. The main standards and terms in the field of nanotechnology are given in the sources [2, 3].

An important component is the concept of the reliability of the measurement results of the characteristics of nanoobjects. The reliability of the results should be formed taking into account GOST (ISO) 17025-2019 General requirements for the competence of research and calibration laboratories. Mandatory fulfillment of these requirements is associated with the inherent properties of nanosystems. These are properties such as:

- the presence of a linear size of objects outside the visible light range (1-100 nm);
- lack of clear phase boundaries;
- comparability of the dimensions of these boundaries with the linear dimensions of nanoobjects;
- uncertainty of the characteristics of nanoobjects.

The uncertainty of measurements is physically related to the variety of conditions and measurement methods and the variability of nanosystems over time, as well as the low reliability of measurement results. The problems of nanometrology are directly related to measuring equipment, calibration, standards and standardized methods.

The obtained multilayer nanoscale coatings based on hafnium and titanium nitrides and their properties should be considered within the framework of TC 441 standards.

To confirm the reliability of the results of research and measurements, should be used the content of GOST (ISO) 17025-2019 General requirements for the competence of research and calibration laboratories.

The measurement results should contain information about deviations of values or ranges of the confidence interval with a given confidence probability. In our opinion, the most acceptable calculation method is the calculation of the interval based on the Student's criterion and the mean square deviation for a given probability. Determining the confidence probability of measurement results, i.e. the inverse problem, has a complicated mathematical apparatus and requires knowledge and skills in the field of mathematical analysis. The measurement results must be obtained on verified, calibrated measuring equipment using standardized methods and in standardized (conditioned) conditions. Using the results of calculating the confidence interval, it is possible to interpret these results with a certain confidence probability. The description of research results should be carried out in terms and definitions recommended by regulatory documents.

During the assessment of the reliability of the results of nano-measurements according to GOST (ISO) 17025-2019 for superhard nanocoats according to GOST R 57408-2017, it is advisable to be guided by the provisions of the standards in the order (protocol): terms, nanoobject, characteristics of nanoobjects, GOST R ISO 22309-2015. GSI. Electron probe microanalysis. Quantitative analysis using energy dispersion spectrometry for elements from 11 and above and GOST R ISO 16243-2016. GSI. Chemical analysis of the surface. X-ray photoelectron spectroscopy. Registration and presentation of data.

And in conclusion, in our opinion, it is useful to pay attention to the terms “nanocoating” and “nanolayer” for composite materials, which are sometimes interpreted equivalently. It is also necessary to observe the difference in the equivalent terms “film” and “coating”, which may not be taken into account when translating.

References
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