Influence of VIP treatment modes on nitride coatings formation with different crystallographic orientation

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Abstract. The change in crystallographic orientation during nitride coatings formation based on titanium and zirconium is studied depending on changes in the concentration ratios for the gas and metal components of the plasma flows and their energy effects on the treated substrate during vacuum ion-plasma (VIP) treatment. It is shown that a decrease in the interaction energy of the gas-metal plasma flow with the surface contributes to the transition of the texture formation of the phase composition to the non-texture.

1. Introduction
Vacuum ion-plasma (VIP) treatment allows forming a wide range of surface composites that combine a wide variety of structural substrates (metallic and non-metallic) and various types of functional coatings that provide a given level of operational properties for engineering products [1]. Composites based on structural materials and coatings formed on the basis of nitride and carbide compounds have received the widest practical application in mechanical engineering.

Properties of such coatings depend primarily on the efficiency of the plasma-chemical reaction on the surface which, in turn, depends on the concentration of coating elements on the substrate and the energy of their interaction as well as on the phase composition formed with a predominant crystallographically oriented [111] direction (textural) with high intensity. Crystallographic planes of the other orientation have too low intensity and high structural instability of their formation, which complicates their use in industrial technologies. This article considers the issues related to a decrease in the texture of the formed coatings, an increase in the intensity and structural stability of the formed additional orientations of planar directions.

2. Method and methodology of the work
Coatings based on Ti-N and Zr-N systems were formed by the electric arc VIP treatment in the process of Ti and Zr plasma flows deposition in 100% N atmosphere on a steel substrate (St1) in the NNV6.6 I1 vacuum ion-plasma facility at the pressure of 0.13 Pa, arc current of 110 A and coating formation time of 60 minutes. The values of the accelerating reference voltage on the substrate were -100 V and -10 V. The interaction of the gas-metal plasma flow with the treated surface was carried out...
after preliminary electron heating of the surface up to 320°C and bombardment by the Ar gas plasma flow for 5 min + 1 min. The heating temperature of the parts in a vacuum chamber was controlled by an IP 140 digital infrared pyrometer. HV microhardness was measured using the Micromet 5101 hardness-testing machine in accordance with GOST R ISO 6507-1-2007 state standard at a load of 0.49 N.

3. Experimental results and discussion
In the process of TiN system coatings formation, accelerating voltage is an important technological parameter that energetically accelerates plasma-chemical processes. The presence of an accelerating reference voltage of (-100 V) on the substrate leads to its heating and activation; at the studied concentration ratio of the components in the gas-metal plasma a compound is formed with predominant [111] planar direction in the TiN interstitial phase and an intensity of the order of 3000, and [222] direction has an intensity of the order of 500 (figure 1). These reflections are most pronounced in this mode of coating formation. Lowering the accelerating voltage to -10 V results in a change in the concentration ratio of the components in the gas-metal plasma and a textureless state formation (figure 2). Such mode of TiN coating formation results in saturation of free bonds on the surface and a structural state with the orientational direction of the [111], [200], [110], [200], [311], [211] planes with intensities less than 250. All the coatings do not have stoichiometric compositions.

**Figure 1.** Diffraction pattern of TiN-based coating formed at $U_{\text{ref}} = -100V$ with strong $\{111\}$ texture and traces of a solid solution. $HV_{0.5} = 41.1$ GPa. $a_{[222]} = 4.265$.

**Figure 2.** Diffraction pattern of TiN-based coating formed at $U_{\text{ref}} = -10V$. Slight traces of a solid solution are observed. $HV_{0.5} = 87$ GPa. $a_{[220]} = 4.270$. 
When ZrN system coatings form, a similar dependence is observed. At a reference voltage of -100 V (figure 3) a textured coating is formed with [111] planar direction with an intensity of the order of 3000, and [200], [311], [222] directions with intensities of less than 1000. A decrease in the accelerating voltage to a value of -10 V leads to the texture with intensities less than 650 (figure 4).

The microhardness of coatings formed at a low reference accelerating voltage is significantly higher than at a traditional one. Thus, the microhardness of the TiN coating increased from 40 GPa to 80 GPa, while the ZrN coating microhardness increased from 30 GPa to 60 GPa.

![Figure 3. Diffraction pattern of ZrN-based coating formed at $U_{\text{ref}} = -100V$. $HV_{0.5} = 31.3$ GPa. $a_{(311)} = 4.608$.](image-url)

![Figure 4. Diffraction pattern of ZrN-based coating formed at $U_{\text{ref}} = -10V$. $HV_{0.5} = 59.5$ GPa. $a_{(220)} = 4.622$.](image-url)

4. Conclusions
Coating formation in the “quiet” mode, when the accelerating voltage on the substrate is minimal and there are no processes of active bombardment of the substrate by plasma elements, promotes the plasma chemistry processes in a wider concentration range with the formation of either non-texture
coatings or those with a low-order texture intensity. Due to the formation of such saturated layers, diffusion processes proceed better, and the thickness of the saturated layer is greater than in diffusion processes at -100V.

The formed coatings have a sufficiently high hardness, and the possibility of their formation at a low accelerating potential makes them promising for processing various products of SMM with complex geometry and sharp edges without overheating the base material and loss of its strength properties.

References
[1] Petrov L M, Grigorovich K V, Ivanchuk S B, Zelenkov V V, Sprygin G S, Smirnova A N and Guseva S S 2017 Scientific works of the Vth International Scientific Conference "Fundamental Research and Innovative Technologies in Mechanical Engineering" (Moscow: IMASH RAN) pp. 201–2