Effect of bias voltage on the texture of the TiN and ZrN coatings deposited by vacuum ion-plasma method

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Abstract. An X-ray diffraction method was used to study the formation of the crystallographic texture of vacuum ion-plasma TiN and ZrN coatings depend on the bias voltage on the substrate. It is shown that, at high values of the bias voltage (-100 V), a pronounced texture forms in TiN coatings and a two-component (111) + (113) texture in ZrN coatings. A decrease of the bias voltage to –10 V leads to a twofold increase in the hardness of the coatings, a non-texture state of TiN, and a weakening of the texture of ZrN coatings.

1. Introduction
It is well known that bias voltage plays a very important role in the deposition process of a coating. A negative bias voltage increases the energy of the ions that bombard the growing coating, which leads to a higher compaction of the coating, an increase in compressive stress and a change in the structure and texture of the coatings [1-6]. The temperature of the substrate is also important, which has a significant effect on the structure and properties of the coatings. In this paper, we investigated the effect of bias voltage on the texture and microhardness of TiN and ZrN coatings deposited by a vacuum ion-plasma method.

2. Materials and methods
Plasma flows of Ti-N and Zr-N systems were formed by electric arc evaporation during vacuum ion-plasma processing. Plasma flows of Ti and Zr were deposited in a 100% atmosphere N on a steel substrate (St1) in an NNV 6.6 I1 vacuum ion-plasma installation at a pressure of 0.13 Pa and an arc current of 110 A; the coating formation time was 60 minutes. The values of the accelerating reference voltage on the substrates were -100V and -10V. The interaction of the gas-metal plasma flow with the treated surface was carried out after preliminary electronic heating of the surface to a temperature of 320°C and its bombardment by a flow of argon gas plasma for 5 min + 1 min. The heating temperature of parts in a vacuum chamber was controlled by an IP 140 digital infrared pyrometer. HV microhardness was measured on a Micromet 5101 microhardness meter in accordance with GOST RISO 6507-1-2007 at a load of 0.49 N. The texture was evaluated by the method of inverse pole figures (IPF) by DRON-3 diffractometer with using CuKα radiation. The pole densities ($P_{hkl}$) for each of the m-poles (hkl) at the IPF were estimated by the ratio of the integrated intensities of the reflexes of the textured ($I_{ml}$) and non-textured reflection ($R_{ml}$, table 1) with Mueller normalization:
3. Results and discussion

In the process of forming coatings based on the TiN system, the bias voltage is an important technological parameter that determines the energy contribution of the gas-metal plasma stream to the acceleration and efficiency of the implementation of plasma-chemical processes of formation of interstitial phases. High values of the bias voltage \( U_{b}=100\text{V} \) leads to an increase in temperature, an increase in the intensity of all processes on the surface of the substrate, which is accompanied by the formation of a pronounced texture (111) in TiN coatings (table 1).

When the bias voltage is reduced to \( U_{b}=-10\text{V} \), a fundamental change in the appearance of the X-ray diffraction pattern of the coating occurs, at which the intensities of all reflections approximately correspond to the non-textured state of the coating. The X-ray diffraction pattern of the ZrN coating at high values of the bias voltage \( U_{b}=100\text{V} \), as in the case of the TiN coating, leads to the formation of a more pronounced texture compared to the coating deposited at a lower value of the bias voltage \( U_{b}=-10\text{V} \). However, unlike the TiN coating, the texture of the ZrN coating is two-component, in addition to the main component (111), similar to TiN, there is a texture (311), the pole density of this component is slightly inferior to the main (111) component (table 1).

A comparison of the pole densities of the main orientations (figures 1a and 2a) for TiN and ZrN coatings shows that the effect of lowering the reference voltage affects the texture of these coatings differently. For TiN coatings, a decrease in the reference voltage to -10 V leads to a textureless state, which is characterized by its deviation \( P_{hkl}\) by no more than 20% (figure 1a, table 1), then for the ZrN coatings these deviations reach 50% (figure 2a, table 1). These differences, however, had almost no effect on the effect of increasing hardness, which increased approximately twice as a result of a decrease in the bias voltage.

The results obtained indicate that a decrease in the bias voltage on the substrate during the deposition of TiN and ZrN coatings eliminates the pronounced (111) texture and significantly increases the hardness of the coatings. A similar effect was obtained when replacing titanium atoms in TiN coatings of Al and Si, which was accompanied by an increase in hardness and corrosion resistance [7-9]. The presence of a pronounced (111) texture is usually associated with the presence of a columnar microstructure, as well as the enlargement of the subgrain structure, estimated by the width of the X-ray diffraction lines[9-12]. It can be assumed that the texture itself is not the reason for the change in properties, i.e. variations in properties are caused not by their anisotropy, but by the fact that, as a result of alloying or changing the energy parameters of the process, the coating formation mechanism changes, which is accompanied by a change in the texture and fine structure of the coating, which is reflected in the level of service properties.

In those cases when, the composition or energy parameters change, the texture remains unchanged is an indication that these changes do not lead to a fundamental change in the mechanism of formation of the coating structure, i.e. essentially, this indicates the ineffectiveness of such changes in terms of optimizing the service properties of coatings.

Thus, the texture is a sensitive structural parameter for evaluating the effectiveness of the search for optimal compositions and technologies for producing coatings, while the texture itself apparently does not

\[ P_{hkl} = \frac{I_{hkl}}{R_{hkl}} \left( \frac{1}{m} \sum_{i=1}^{m} \left( \frac{I_{hkl}}{R_{hkl}} \right) \right) \]
significantly affect the properties, since most coatings have highly symmetric crystal structures, in most cases a cubic NaCl lattice. For cubic crystals, even in the case of a sufficiently high single-crystal anisotropy, it is difficult to realize a substantial anisotropy of properties even in a highly textured polycrystal due to the high multiplicity factors of most crystallographic orientations (up to 48) and the presence of an obligatory region of texture spread, especially in the case of two or more texture components. In the latter case, the absence of anisotropy of properties is inevitable.

Figure 1. Pole reflection densities (a) and hardness values (b) for TiN coatings obtained by the vacuum-arc method at substrate voltages of -100 and -10 V.

Figure 2. Pole reflection densities (a) and hardness values (b) for ZrN coatings obtained by the vacuum-arc method at substrate voltages of -100 and -10 V.

4. Conclusions
1. A high value of the bias voltage (-100 V) leads to the intensification of processes on the surface of the substrate, which is accompanied by the formation of a pronounced texture (111) in TiN coatings and a double texture (111) + (113) in the ZrN coating.
2. A decrease in the bias voltage leads to a twofold increase in the hardness of the coatings, a non-texture state of TiN, and a weakening of the texture of ZrN coatings.

5. References
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