Physical and mechanical properties of nanostructured (Ti-Zr-Nb)N coatings obtained by vacuum-arc deposition method

Abstract. By vacuum-arc evaporation of multielement Ti+Zr+Nb cathode in nitrogen atmosphere, (Ti-Zr-Nb)N coatings have been deposited on steel substrates. The coatings are characterized by a columnar structure with nanosized (10-63 nm) crystallites of the main FCC nitride phase (Ti-Zr-Nb)N. Such coatings seem to have promising properties for applications as protective coatings.

X-ray diffraction studies of the samples with coating was carried out on diffractometer DRON-4 in Cu-Kα radiation in the pointwise mode scanning step 2θ = 0.05°. The microhardness measurements were carried out by using an automatic system for analysis of DM-8 microhardness with a load on the indenter 0.05 H by the micro-Vickers method.

Results and discussion

Adhesion-cohesive strength, scratch resistance and failure mechanisms of coatings were performed on the air using a scratch tester Revetest (CSM Instruments).

The tribological tests were carried out in air in a “ball-ROM” drive friction Tribometer (CSM Instruments). To this coating with thickness 4.0 microns was deposited on the polished surface (Rₕ = 0.088 mm) of the samples in the form of discs made of steel 45 (HRC = 55) with a diameter 42 and a height of 5 mm. As counterbody the ball with diameter 6.0 mm was used, it is made of sintered material certified - Al₂O₃. The load was 3.0 H, the sliding speed of 10 cm/s. Test conditions meet international standards ASTM G99-959, DIN50324 and ISO 20808.

The roughness and the amount of coating material removed was determined by the cross section of track wear on the surface of a sample with an automated precision contact profilometer model Surtronic 25. The structure of the groove wear coating and wear and tear on the spot beads were investigated optical inverted microscope Olympus GX 51 and the scanning ion-electron microscope Quanta 200 3D. As a result of the wear tests evaluated factor [14] coated sample and statistical partner (ball) as described in [15].

Results and discussion

Image surface of the coatings as well as fractogram fracture showned on Figs. 1 and 2.
This is particularly important at presence in the vacuum chamber of reactive gases, forming with vaporizable material refractory compound. Also, it is observed a decrease in the roughness of the coating.

The elemental composition of coatings produced by vacuum arc deposition was analyzed by energy dispersive method (Table 2).

If you compare the elemental composition of the coatings used in the series, it can be seen that the samples of the first series of the number of nitrogen atoms is almost identical. For a series of samples obtained at a higher pressure N₂ atmosphere, characterized by a significant increase in the proportion of zirconium atoms and a decrease in the proportion of titanium atoms.

The content of niobium atoms samples of both series remains virtually unchanged. Increasing the content of titanium atoms in the condensates B series is explained, it seems to be more effective interaction with the nitrogen atom of titanium in the surface region.

Table 2. Chemical composition of elements in the coating (Ti-Zr-Nb)N

<table>
<thead>
<tr>
<th>Series</th>
<th>Elemental composition, at.%</th>
</tr>
</thead>
<tbody>
<tr>
<td>N</td>
<td>Ti</td>
</tr>
<tr>
<td>A</td>
<td>38.72</td>
</tr>
<tr>
<td>B</td>
<td>40.00</td>
</tr>
<tr>
<td>C</td>
<td>40.86</td>
</tr>
</tbody>
</table>

Investigation of fractogramm fracture surfaces (Fig.2) obtained at different partial pressures of nitrogen, indicating the formation of the columnar structure (Fig.2b), the characteristic of coating produced by vacuum-arc deposition.

The analysis X-ray diffractometer spectra on Fig.3 shows that as the determining phase composition is the phase with a face-centered cubic lattice. Low-intensity peak at $2\theta = 38^\circ$ indicates the presence of small inclusions with BCC lattice, typical for vacuum-arc method for dropping phase [16].

It should be noted that with increasing of pressure the intensity of this peak decreases (see the spectra 1 and 3 on Fig.3), which determined by a significant decrease of content in the droplet phase in the coating and correlates with the results of surface examination.

A characteristic feature with increasing pressure of the reaction gas is strengthening the peaks of the family of planes {111}, which is determined by the increase of perfection preferred orientation of growth of crystallites with [111] axis perpendicular to the plane of the surface. Specific method of approximating the size of the crystallites with an increase in pressure increases from 10 nm at the lowest pressure of $3\times10^{-4}$ Torr to 63 nm at the maximum working pressure nitrogen atmosphere $4\times10^{-3}$ Torr.

The study results of the adhesive-cohesive strength, scratch resistance of coatings shown on Fig.4 and Fig.5. On the basis of the graphs the change of the friction coefficient and acoustic emission from the load of scribing determined the following main critical loads: $L_{C1}$ – the emergence of the first chevron cracks on the bottom and diagonal around the edges of crack; $L_{C2}$ – the formation of a plurality of chevron cracks on the bottom of the crack and local peeling of coating, appearing of chevron cracks on the bottom of the crack; $L_{C3}$ – cohesively-adhesion failure of the coating; $L_{C4}$ – plastic abrasion of the coating.
Fig. 3. Areas of the diffraction spectra of coatings obtained at different partial pressure of nitrogen: curve 1 – \( P = 3 \times 10^{-4} \) Torr; 2 – \( P = 7 \times 10^{-4} \) Torr; 3 – \( P = 4 \times 10^{-3} \) Torr; identified planes of FCC lattice

Fig. 4. Dependence of friction coefficient on the applied load at a scratch test of the coating \((Ti-Zr-Nb)N\), obtained at \( P = 4 \times 10^{-3} \) Torr

Conventionally, the process of destruction of the coating in scratching with the indenter can be divided into four stages. At the load range of \( F = 0.9 \) H to \( F = 9.89 \) H appears the monotonically penetration of the indenter into the coating: the friction coefficient slightly increases the acoustic emission signal remains unchanged. When the load \( F = 15.81 \) H indenter is completely immersed in the coating. Slipping diamond indenter for cover run with friction coefficient 0.35.

Important parameter governing performance coatings are also its tribological properties (coefficient of friction and wear factor). The friction coefficient \( \mu \) defines a traction friction material and the factor of wear - wear resistance (less than a factor wear, the better the durability).

As the load increases (\( F = (20.6 – 36.4) \) H) occurs the extrusion of the material before the indenter as hillocks and increased the penetration depth of the indenter.

Table 3 shows the results of tests of samples with coatings \((Zr-Ti-Nb)N\) coatings in comparison with the \((Ti-Zr-Si)N\) and TiN obtained by us [17].

<table>
<thead>
<tr>
<th>Critical loads</th>
<th>((Zr-Ti-Nb)N) series a</th>
<th>((Zr-Ti-Nb)N) series b</th>
<th>((Zr-Ti-Nb)N) series c</th>
<th>((Ti-Zr-Si)N)</th>
<th>TiN</th>
</tr>
</thead>
<tbody>
<tr>
<td>( L_{C1} )</td>
<td>2.91</td>
<td>0.9</td>
<td>9.89</td>
<td>3.91</td>
<td>21.31</td>
</tr>
<tr>
<td>( L_{C2} )</td>
<td>29.04</td>
<td>15.82</td>
<td>20.62</td>
<td>18.15</td>
<td>30.91</td>
</tr>
<tr>
<td>( L_{C3} )</td>
<td>43.18</td>
<td>42.37</td>
<td>36.43</td>
<td>24.29</td>
<td>40.28</td>
</tr>
<tr>
<td>( L_{C4} )</td>
<td>59.26</td>
<td>66.24</td>
<td>66.77</td>
<td>43.15</td>
<td>48.84</td>
</tr>
</tbody>
</table>

As criteria of the adhesion strength was accepted critical load \( L_{C4} \), leading to abrasion of the coatings. Fig. 4 shows the dependence of the friction coefficient and acoustic emission signal from the applied load at scratch test samples of series B.

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All coated samples (series A, B, C), the friction coefficient was higher than 1.0. Such high values may be explained by the high roughness (Fig. 1), associated with the presence at the surface and in the coating of the droplet fraction formed by vacuum-arc deposition. The appearance of a solid component of dropping and formation of degradation during the coating of wear in the form of particles consisting of hard nitrides, leads to abrasion of the coating.

Reducing the surface roughness decreases with a coefficient of friction of 1.95 to 1.05. With the increase in the hardness of the coating wear factor \( W \) coating decreases and counterbody – increased. With the increasing of pressure and the appearance of preferential orientation of crystallite growth with the axis [111] (Fig. 2) observes a decrease in the setting and wear material, which correlates with the previously established increase in hardness with increasing pressure of nitrogen during deposition of the coating. These results can be explained by an increase in the packing density of the atoms (111) plane of the FCC lattice [18], which increases the hardness cover, as the introduction of the indenter in the axis of the texture in the coating [111] is perpendicular to these planes. Increased resistance wear in this case is determined by the wear that in the process of wear occurs removal of a solid layer-planes (111) of a material that minimizes destruction.

**Conclusions**

1. With method of vacuum arc evaporation solid cathode in the medium of reaction gas nitrogen obtained nanostructured coating of \((Ti-Zr-Nb)N\). Multicomponents films have a pronounced columnar structure.

2. Elemental composition of obtained with vacuum-arc deposition coatings \((Ti-Zr-Nb)N\) depends on the physico-technological parameters, by precipitation, particularly on the pressure of the reaction gas nitrogen.
3. From X-ray analysis follows that the main phase is a face-centered cubic lattice. With the increasing of the pressure dimensions of nanocrystals increases from 10 nm at the lowest pressure of $3 \times 10^{-4}$ Torr to 63 nm at the maximum working pressure nitrogen atmosphere $4 \times 10^{-3}$ Torr.

4. Investigation of the effect of physical and technological parameters of deposition on the hardness of coatings. The hardness of the coatings of (Ti-Zr-Nb)N system, obtained at a partial pressure of $P = 4 \times 10^{-3}$ Torr is $H_{\text{HV}} = 44.57$ GPa, and at a pressure $P = 3 \times 10^{-3}$ Torr hardness is $H_{\text{HV}} = 37.21$ GPa.

5. The adhesion strength of coatings based on (Ti-Zr-Nb)N markedly higher compared to coatings based on (Ti-Zr-Si)N and TiN, and the adhesion failure is observed at the load $F = 66.77$ GPa for coating (Ti-Zr-Nb)N for coating based on (Ti-Zr-Si)N $F = 48.84$ GPa; and for TiN $F = 55.2$ GPa.

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