Structures and Properties of Vacuum-arc Coatings of Chromium and Its Nitrides Obtained under the Action of Constant and Pulse High-voltage Bias Potential


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To reveal the regularities of structural engineering of vacuum-arc coatings based on chromium and its nitrides, the influence of the main physico-technological factors (the pressure of the nitrogen atmosphere and the bias potential) in the formation of coatings was studied. It was discovered that during the deposition of chromium coatings the formation of the texture axis [001], as well as the macrodeformation of compression is happening. The supply of a high-voltage negative pulse potential to the substrate increases the mobility of the deposited atoms and leads to relaxation of the compression deformation. As the pressure increases from 2.10^{-1} Torr to 4.8.10^{-3} Torr, the phase composition of the coatings changes: Cr (JCPDS 06-0694) → CrN (JCPDS 35-0803) → CrN(JCPDS 11-0065). The supply of high-voltage pulses leads to the formation of a texture of crystallites with parallel growth surfaces planes having d ≈ 0.14 nm. The structure obtained by pulsed high-voltage action makes it possible to increase the hardness of the coating to 32 GPa and reduce the friction coefficient to 0.32 in the “chromium nitride-steel” system and to 0.11 in the “chromium nitride-diamond” system.

The results obtained are explained from the viewpoint of increasing the mobility of atoms and the formation of cascades of displacements when using an additional high-voltage potential in the pulse form during the deposition of chromium-based coatings.

Keywords: Vacuum arc, Cr, CrN, Pressure, Bias potential, Pulse potential, Phase composition, Structure, Hardness, Friction coefficient.

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1. INTRODUCTION

It is known that an increase of the ionic component in the flow of deposited particles leads to a significant change in the structure and properties of the coatings obtained [1]. It was found that the functional characteristics of the coatings depend significantly on the phase composition [2], the structure of the coatings [3], the degree of texturization [4], and the stress-strain state [5]. The use of nitrogen ions as charged particles made it possible to form coatings of nitrides, the performance characteristics of which significantly exceed the analogous properties of metals [6].

Coatings based on chromium nitride are of interest, both for basic research and for applied use, taking into account the high functional properties in nitride chromium. Thus, CrN coatings are one of the widely used as protective in such areas as automotive, aerospace industry [7], for die and mould, mechanical components, and artificial joints to increase their service life due to their excellent oxidation resistance, corrosion resistance, low friction coefficient, and high wear resistance [8-12].

At this point, the properties of Cr-N coatings depend in a determined manner on their structure, and, consequently, on the method for their preparation.
2. EXPERIMENTAL DETAILS

The coatings were deposited in the modernized vacuum-arc unit "Balat-6" [1]. Cr was used as the cathode material with a purity of 99.95%. The active gas is nitrogen (99.9 %). To obtain chromium coatings, the pressure in the vacuum chamber did not exceed 2 · 10⁻⁵ Torr during deposition, and when the coatings of chromium nitride were deposited, the pressure of the nitrogen atmosphere was \( P_N = (3.5 \cdot 10^{-4} \ldots 4.8 \cdot 10^{-4}) \) Torr. During deposition, a constant negative potential was applied to the substrate with a value of \( U_S = -30, -60, -110 \) and \(-170 \) V. In order to avoid overheating of the substrate and a substantial increase in the mobility of atoms in deposition [19], a high potential \( U_{HV} \) with an amplitude of 2 kV in a pulsed mode with a frequency of 7 kHz and a duration of 10 μs (corresponding to \( \approx 7 \% \) of the total application time) was applied. The duration of the deposition process was 1 to 2 hours. The plates were used as substrates and were made of stainless steel 12X18N10T with dimensions 18 × 18 × 2 mm and copper foils.

The phase composition, structure, and substructural characteristics were studied by the X-ray diffractometry (DRON-4) using Cu-Kα radiation. To monochromatize the detected radiation, a graphite monochromator was used, which was installed in a secondary spectrometer (in front of the detector). The phase composition, structure, and substructure characteristics were studied using traditional X-ray diffractometry techniques by analyzing the position, intensity, and shape of the diffraction reflection profiles. To decode the diffractograms, the tables of the international diffraction data center Powder Diffraction File were used.

Microindentation was carried out at the «Micron-gamma» unit with a load up to \( F = 0.5 \) N with a Berkovich diamond pyramid with an angle of sharpening 65°, with automatic loading and unloading for 30 seconds [20]. The study of the wear resistance characteristics was carried out on the "Micronfriction" device by rotating a diamond indenter with a radius of curvature of approximately 500 μm along the coating circle. In the automatic mode, the load level \( (P) \) and the frictional force between the diamond surface and the coating \( (F) \) were recorded. The friction coefficient \( (\mu) \) was determined as a result of the ratio of the frictional force to the load.

3. RESULTS AND THEIR DISCUSSION

Let us consider the results of the influence of two main parameters responsible for the energy state of the deposited particles (negative bias potential in a constant and high-voltage pulse forms) on the structural-phase changes in the coatings obtained by vacuum-arc evaporation of pure chromium in high vacuum (at a pressure of 2 · 10⁻⁵ Torr). The deposited in such way coatings are effectively used for protection of bearings of heavy-loaded elements of gas turbine aggregates and other elements [21].

In the way of revealed regularity by the analysis of the diffraction spectra of the coatings (Fig. 1), it can be noted that at a pressure of 2 · 10⁻⁵ Torr for the entire \( U_b \) interval, the single-phase state of Cr with the volumecentered, bcc crystal lattice (JCPDS 06-0694) is formed. All coatings are strongly textured with the axial texture axis [100]. With the greatest displacement potentials, the formation of the second texture axis [110] is revealed and thus the formation of a biaxial state (Fig. 1 a, b, spectrum 1). The period of the lattice of coatings obtained at low \( U_b \) was close to the tabulated 0.2883 nm, and at a large \( U_b \) it increased to 0.2886 nm. In a single-element and single-phase material, the cause of such a change can be the formation of a stress-strain compression state [5]. Evaluation of the macrodeformation gives a compression value of \( \approx 0.43 \% \). It should be noted that, along with \( U_b \), the supply of a high-voltage bias potential in pulse form (amplitude 2 kV, duration 10 μs, which is \( \approx 7 \% \) of the time from the total exposure time) does not qualitatively change the general form of the spectra. However, there is no increase in the period for large \( U_b \) in this case. The results obtained show that as a result of high-voltage pulse action (this leads to an increase in energy and the formation of cascades in the deposition of particles), the mobility of the particles increases, which leads to relaxation of compression deformation.

In this case, as was established by analyzing the width of the diffraction profiles [3], the crystallite size in the coatings with increasing \( U_b \) tends to increase to \( U_b = -110 \) V (without \( U_{HV} \) feed) with a further drop to an average size of about 30 nm at the largest \( U_b = -170 \) V (Fig. 2, spectrum 1). At small \( U_b \) under the conditions of \( U_{HV} \) action, the average crystallites size is much larger (up to 38 nm), which may be due to greater mobility of the atoms deposited under the action of \( U_{HV} \).
the average size of crystallites in Cr coatings obtained at a pressure of $3 \times 10^{-3}$ Torr and different constant bias potentials on the substrate ($U_b$) without additional high-voltage pulse action (1) and with additional pulse action with an amplitude of 2 kV and a frequency of 7 kHz (2).

With increasing pressure ($P_N$), nitride phases are formed. At $P_N = 3.5 \times 10^{-4}$ Torr, the main nitride phase is $\beta$-Cr$_2$N (JCPDS 35-0803) with a hexagonal type of crystal lattice (Fig. 3). With increasing $U_b$, a texture of the crystallites with a texture plane (111) is formed (Fig. 1, a, b, spectrum 2).

Fig. 2 – The change in the average size of crystallites in Cr coatings obtained at a pressure of $2 \times 10^{-3}$ Torr and different constant bias potentials on the substrate ($U_b$) without additional high-voltage pulse action (1) and with additional pulse action with an amplitude of 2 kV and a frequency of 7 kHz (2).

At a pressure of $P_N = 1.3 \times 10^{-3}$ Torr, the formation of the CrN phase occurs (JCPDS 11-0065).

Comparison of the diffraction spectra for different $P_N$ coatings obtained under the action of a large $U_b = -110$ V without and with $U_{\text{HVP}}$ (Figure 4) showed that at the lowest pressure ($3.5 \times 10^{-4}$ Torr) a two-phase state forms. The crystallites of the phases are textured with the most densely packed planes parallel to the growth plane: (110) Cr and (111) $\beta$-Cr$_2$N (Fig. 4a). Note that the $U_{\text{HVP}}$ supply additionally stimulates the formation of (300) $\beta$-Cr$_2$N texture with a characteristic interplanar spacing of 0.14 nm (spectrum 2 in Fig. 4a). When the pressure is raised to $7.5 \times 10^{-4}$ Torr, the texture with the plane (300) $\beta$-Cr$_2$N becomes the main one, and the coatings are formed practically in a single-phase state. When the pressure is increased to $1.8 \times 10^{-3}$ Torr (Fig. 4c), the already almost single-phase state is formed on the basis of the CrN phase with the cubic lattice and with the texture plane (220). It is interesting to note that the interplanar distance parallel to the plane of the surface is also about 0.14 nm. At the maximum pressure of $4.8 \times 10^{-3}$ Torr (Fig. 4d), under the action of $U_{\text{HVP}}$, the texture (220) is amplified (spectrum 2), and without $U_{\text{HVP}}$ supply, coatings are formed with the standard texture (111) for FCC lattice at these pressures [4].

Fig. 3 – The arrangement scheme of atoms and vacancies in the hexagonal crystal lattice of the $\beta$-Cr$_2$N phase.

Fig. 4 – Areas of diffraction spectra of chromium nitride coatings obtained at $U_b = -110$ V without (1) and with $U_{\text{HVP}}$ (2) at different $P_N$, Torr: a – $3.5 \times 10^{-4}$, b – $7.5 \times 10^{-4}$; c – $1.8 \times 10^{-3}$; d – $4.8 \times 10^{-3}$.

At a sub-structural level under similar formation conditions, the crystallite sizes in the coatings obtained without $U_{\text{HVP}}$ are 10-15% less than in coatings obtained with $U_{\text{HVP}}$. At the maximum pressure, their size
reaches 14 nm, and the value of the microdeformation is \(<\varepsilon> \approx 0.26\%\).

The most universal characteristic that determines the mechanical properties of the coating is hardness. The results of microindentation of chromium nitride coatings obtained at different \(P_n\) are given in Table 1.

<table>
<thead>
<tr>
<th>(U_{hv}) V</th>
<th>(U_{hv}) kV</th>
<th>(P_0) mTorr</th>
<th>(H) GPa</th>
<th>(H/E^*)</th>
<th>(E^*) GPa</th>
<th>(E) GPa</th>
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<tbody>
<tr>
<td>-110</td>
<td>-</td>
<td>4.8</td>
<td>20</td>
<td>0.092</td>
<td>216</td>
<td>256</td>
</tr>
<tr>
<td>-110</td>
<td>-</td>
<td>1.8</td>
<td>25.5</td>
<td>0.117</td>
<td>216</td>
<td>255</td>
</tr>
<tr>
<td>-110</td>
<td>-</td>
<td>0.75</td>
<td>25.5</td>
<td>0.103</td>
<td>247</td>
<td>302</td>
</tr>
<tr>
<td>-110</td>
<td>-</td>
<td>0.35</td>
<td>20.5</td>
<td>0.097</td>
<td>209</td>
<td>246</td>
</tr>
<tr>
<td>-110</td>
<td>-2</td>
<td>4.8</td>
<td>27</td>
<td>0.114</td>
<td>236</td>
<td>286</td>
</tr>
<tr>
<td>-110</td>
<td>-2</td>
<td>1.8</td>
<td>29</td>
<td>0.111</td>
<td>260</td>
<td>324</td>
</tr>
<tr>
<td>-110</td>
<td>-2</td>
<td>0.75</td>
<td>32</td>
<td>0.112</td>
<td>285</td>
<td>364</td>
</tr>
<tr>
<td>-110</td>
<td>-2</td>
<td>0.35</td>
<td>28</td>
<td>0.090</td>
<td>308</td>
<td>405</td>
</tr>
</tbody>
</table>

It can be seen that the use of the pulse potential \(U_{hv}\) leads (at comparable production conditions) to a significant increase in hardness. The highest values of hardness are inherent in coatings obtained in the interval \(P_n = (7.5 \times 10^{-4}...1.8 \times 10^{-3})\) mTorr.

It should also be noted that for the hardest coatings, the ratio \(H/E^* \approx 0.11\) (\(H\) is hardness, \(E^*\) is the reduced elastic modulus, Table 1).

The second important mechanical characteristic that determines the performance of the coating is its wear resistance. As a rule, coatings with the greatest possible hardness, adhesion and minimum friction coefficient have the smallest wear [22]. Thus, one of the indicators of wear resistance is the friction coefficient. To determine it, the method of rotation of the loaded indenter was used in the work.

Figure 5 shows the surface photographs and the 3D profile of the groove and the friction surface.

Tribological tests were carried out for two types of pairs "chromium nitride - steel ShKh" and "chromium nitride – diamond". Figure 6 shows the results of such tests, made depending on the hardness of the coatings. It can be seen that, for chromium-based nitride coatings, there is a tendency to reduce the friction coefficient with increasing stiffness in pairing with steel ShKh (Fig. 6, curve 1) and stability of the friction coefficient in pair with diamond (Fig. 6, curve 2). In absolute magnitude, in the first case, the friction coefficient is 0.32, and in the second, about 0.12.

![Fig. 5](image)

![Fig. 6](image)

**Fig. 5** – Photographs of the friction surface (a), the groove depth scanning curve (b) and the 3D groove profile and the friction surface (c) of the chromium nitride samples

**Fig. 6** – Dependence of the friction coefficient of the coating on the basis of chromium nitride in pair with steel ShKh (1) and diamond (2)

The obtained test results are quite predictable. The low friction coefficient in the case of a pair of "chromium nitride – diamond" is determined by the possibility of forming on the contacting surfaces of the carbon layer (serves as a solid lubricant). In the case of a pair of "chromium nitride – steel ShKh", such a lubricant is not formed, the friction meets the rigid conditions of solid-state contact.

**4. CONCLUSIONS**

Thus, the X-ray structural analysis of coatings in combination with the study of tribological characteristics (tribology can be defined as the science of surface layers strength of solid materials with their relative displacement) showed that in the hardest and most wear-resistant coatings of chromium nitride (with the lowest friction coefficient) CrN crystallites with plane orientation (220) are parallel to the working surface.
Структура і властивості вакуумно-дугових покриттів хрому і його нітридів, отриманих в умовах дії постійного і імпульсного високовольтного потенціалів зсуву

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Для виявлення закономірностей структурної інженерії вакуумно-дугових покриттів на основі хрому та його нітридів досліджено вплив основних фізико-технологічних факторів (тиск азотної атмосфери і потенціал зсуву) при формуванні покриттів. Встановлено, що при осадженні покриттів хрому відбувається формування: осі текстури [100], а також макродеформації. Подача високовольтового негативного імпульсного потенціалу на підкладку підвищує рухливість атомів, що осаджуються і призводить до релаксації деформації структури. Зі збільшенням тиску від 2·10−3 Торр до 4,8·10−3 Торр фазовий склад покриттів змінюється: Cr (JCPDS 06-0694) → CrN (JCPDS 35-0803) → Cr2N (JCPDS 11-0065). Подача високовольтових імпульсів призводить до формування текстиури кристаллітів з паралельними поверхні структурно зштовхуваними плоскостями, що мають ≈ ± 0.14 нм. Одержані від імпульсного високовольтного впливу структури дозволяю підвищити твердість покриттів до 32 ГПа і знизити коефіцієнт тертя до 0.32 в системі «нітрид хрому – сталь» і до 0.11 в системі «нітрид хрому – алмаз».

Ключові слова: Вакуумна дуга, Cr, CrN, Тиск, Potенціал зсуву. Імпульсний високовольтний потенціал, Фазовий склад, Структура, Твердість, Коефіцієнт тертя.

Структура і свойства вакуумно дугових покритий хрома і нітридів, отриманих в умовах дії постійного і імпульсного високовольтного потенціалів смаєння

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Для установления закономерностей структурной инженерии вакуумно-дуговых покрытий на основе хрома и его нитридов изучено влияние основных физико-технологических факторов (давления азотной атмосферы и потенциала смещения) при формировании покрытий. Установлено, что при осаждении покрытий хрома происходит формирование оси текстуры [100], а также макродеформация. Подача високовольтового отрицательного потенциала на подложку повышает подвижность осаждаемых атомов и приводит к релаксации деформации структуры. С увеличением давления от 2·10−3 Торр до 4,8·10−3 Торр фазовый состав покрытий изменяется: Cr (JCPDS 06-0694) → Cr2N (JCPDS 35-0803) → CrN (JCPDS 11-0065). Подача высоковольтных импульсов приводит к формированию текстуры кристаллитов с параллельными поверхностями, имеющими d0 0.14 нм. Полученная при импульсном высоковольтном воздействии структура позволяет повысить твердость покрытия до 32 ГПа и понизить коэффициент трения до 0.32 в системе «нитрид хрома – сталь» и до 0.11 в системе «нитрид хрома – алмаз».

Полученные результаты объясняются с позиции повышения подвижности атомов и образования каскадов смещений при использовании в процессе осаждения покрытий на основе хрома дополнительно высоковольтного потенциала в импульсной форме.

Ключевые слова: Вакуумная дуга, Cr, CrN, Давление, Потенциал смещения, Импульсный высоковольтный потенциал, Фазовый состав, Структура, Твердость, Коэффициент трения.
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