

Regularities of Structure Formation of CrN Coatings Obtained by Vacuum Arc Evaporation in a Nitrogen Atmosphere

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The questions of structural engineering of Cr-N system coatings produced by vacuum arc evaporation of Cr cathode in a nitrogen atmosphere are considered. As the variable physical and technological parameters we have used the following ones: pressure of nitrogen atmosphere $(3.5..48) \cdot 10^{-4}$ Torr and negative bias potential applied to the substrate in constant ($U_b = -120$ V) and pulse ($U_{ip} = -1200$ V) modes.

Increase in the pressure without pulse action allows to transfer from Cr + Cr₂N phase to phase of textured CrN crystallites with [111] axis. The transition from the metallic phase to the mechanical nitride is accompanied by a decrease in the average size of crystallites. Additional supply of impulse capacity allows to intensify the process of formation of nitrides and stimulates formation at high pressures of radiation-resistant texture units with the [110] axis.

Keywords: Vacuum-arc method, Pressure, CrN, Texture, Substructure, Intensity, Size of crystallites.

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1. INTRODUCTION

At present, more and more attention is paid to the connection between the deposition conditions and coating structure, since coatings are one of the most efficient tools for providing the necessary functional properties to the surface (surface engineering). Use of high-production vacuum-arc method allows to obtain the coating materials which can operate in conditions of high temperatures and pressures under the action of corrosive media and intensive wear. Chromium nitride (CrN) belongs to the number of the most promising materials proving high wear and corrosion resistances of the edge tools operating at high cutting speeds [1-3]. Moreover, CrN exhibits high temperature stability and has lower friction coefficient than TiN, which currently is the most widely used in industry [4-7].

Average energy of particles forming the coating is one of the most important physical and technological parameters of the surface engineering at deposition. Larger energy value leads to the increase in the mobility of atoms on the surface at deposition [8-10]. For equal deposition rates, the greater mobility of atoms, the more intense diffusion that allows atoms to penetrate deeper and also leads to the coalescence [11]. Thus, for higher energy values of the deposited particles, one observes the changes in the surface and texture morphology resulting in the formation of the films with larger grains and smaller defects. Increase in the grain size is often accompanied by deterioration of the mechanical properties. In order to avoid this effect, high-energy impact is realized in the pulse mode. Smoothing of the growth plane, stabilization of the small-size state of crystallites, change of the texture axis and relaxation of the growth voltages take place in this case [12, 13].

In this work, the change of the energy parameters of particles at deposition of CrN coatings was achieved by different pressures of nitrogen atmosphere in deposition

and by the application of a negative bias potential to the substrate. In order to avoid the substrate overheating and significant increase in the grain size at deposition, a relatively low constant potential less than -120 V was used and higher potential -1200 V was applied in the pulse mode with the frequency of 7 kHz and action time of 10 μ s.

2. MODES OF COATINGS PRODUCTION AND INVESTIGATION TECHNIQUES

To solve the problem of structural engineering at the modernized plant "Bulat-6" additionally equipped by the high voltage pulse generator (pulses are delivered to the substrate during deposition), we have obtained the CrN coatings in the pressure range of a nitrogen atmosphere $P_N = (3.5 \cdot 10^{-4}..4.8 \cdot 10^{-3})$ torr, for the constant negative bias potential applied to the substrate $U_b = -120$ V and high-voltage potential $U_{ip} = 1.2$ kV applied in the pulse mode with the frequency of 7 kHz and the action time of 10 μ s ($\sim 7\%$ of the total deposition time). Duration of the deposition process was equal from 1 to 2 hours. As the substrates, plates of the stainless steel 12X18H10T of the sizes of $18 \times 18 \times 2$ and copper foils were used.

Structural investigations of the samples were carried out by the X-ray structural analysis on the plant "DRON-3M". Cu-K α radiation was used in all the investigations. In order to determine the orientation dependence of the coatings, the survey was realized with the Bragg-Brentano focusing in the θ - 2θ configuration. The average size of crystallites was determined by the broadening of the diffraction reflexes using the Selyakov-Scherrer equation.

3. RESULTS AND DISCUSSION

For the analysis of the influence of the physical and technological parameters of the vacuum-arc method on the structure and substructural state of CrN coatings,

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we have obtained the samples at different pressures of a nitrogen atmosphere (as the key parameter) under the action of the constant negative substrate potential ($U_b = -120$ V), as well as the additional high-voltage pulse action ($U_{ip} = -1200$ V). X-ray diffraction spectra of the coatings without a pulse action are shown in Fig. 1 and under the additional pulse action – in Fig. 2.

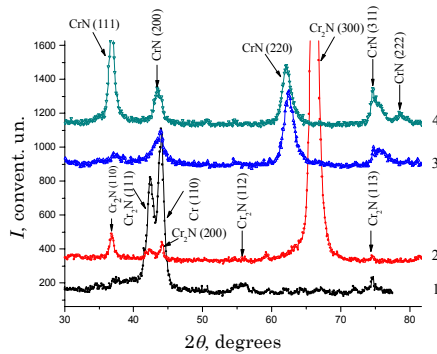


Fig. 1 – Diffraction spectral regions of the coatings of the Cr-N system obtained at $U_b = -120$ V; P_N , torr: 1 – $3.5 \cdot 10^{-4}$; 2 – $7.5 \cdot 10^{-4}$; 3 – $1.8 \cdot 10^{-3}$; 4 – $4.8 \cdot 10^{-3}$

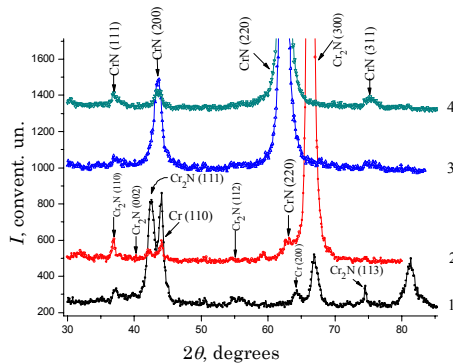


Fig. 2 – Diffraction spectral regions of the coatings of the Cr-N system obtained at $U_b = -120$ V; $U_{ip} = -1200$ V; P_N , torr: 1 – $3.5 \cdot 10^{-4}$; 2 – $7.5 \cdot 10^{-4}$; 3 – $1.8 \cdot 10^{-3}$; 4 – $4 \cdot 10^{-3}$

Amplification of the relative intensity of reflections from the plane (220) at the highest deposition pressure of $4.8 \cdot 10^{-3}$ torr (Fig. 2, spectrum 4) is the distinctive feature of the pulse action in contrast to the appearance of the pronounced texture (111) in the absence of high-voltage impact (Fig. 1, spectrum 4).

The same amplification effect of (220) is exhibited at the pressure of $1.8 \cdot 10^{-3}$ torr (Fig. 2, spectrum 3), however, in this case besides the main texture with the axis [110] perpendicular to the growth plane, the formation of crystallites with the second type of the texture with the axis [100] takes place.

For smaller pressure of a nitrogen atmosphere of $7.5 \cdot 10^{-4}$ torr, Cr_2N phase with the texture axis [100] is the main phase both in the case of the pulse action and without it. We note that at additional pulse stimulation, CrN phase with the texture axis [110] is formed (Fig. 2, spectrum 2, region $2\theta = 60 \dots 65^\circ$). That is at such a pressure, pulse high-voltage stimulation increases the efficiency of nitride formation during the interaction with nitrogen of the working atmosphere and simultaneously leads to the formation of the texture axis [110] perpendicular to the growth surface.

Analysis of the diffraction spectra of the coatings deposited at the lowest pressure of $3.5 \cdot 10^{-4}$ torr has shown that pulse action stimulates a more efficient nitride-formation in this case as well, although here it has a disorienting effect on the growth of crystallites leading to the formation of almost non-textured coating. In this case, the Cr phase with the texture axis [110] and Cr_2N phase with the axis [111] are formed in the absence of the pulse action (Fig. 1, spectrum 1). Specific content of the Cr_2N phase increases during the pulse stimulation. At that, the degree of texture [111] perfection of Cr_2N significantly decreases and formation of the second axis of the radiation-stimulated texture [100] occurs (Fig. 2, spectrum 1). Decrease in the degree of texture perfection under the high-voltage pulse action can be associated with the occurring here cascade-formation process in the near-surface region of the coating growth, since energy loss in collisions are insignificant at low pressures, and particles bombard the growing surface with the highest energy sufficient for the formation of cascades [14].

As it follows from the obtained results, formation of the single-phase CrN coatings takes place in the case of a larger pressure ($P_N = 4.8 \cdot 10^{-3}$ torr) (Fig. 3, spectra 3 and 4). Texture with the axes [111] and [110] is formed in the pulse-free mode. Pulse high-voltage action stimulates the growth of texture [110] perfection. Reflexes inherent in the phases of pure Cr and Cr_2N are revealed on the X-ray diffraction spectra (Fig. 3, spectra 1 and 2) at the lowest pressure $P_N = 3.5 \cdot 10^{-4}$ torr that indicates a weak interaction of nitrogen with chromium. Increase in the amount of the Cr_2N phase is the distinctive feature of the coatings obtained in the pulse stimulation.

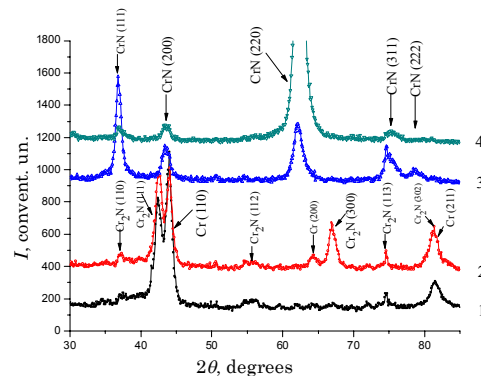


Fig. 3 – Diffraction spectral regions of the coatings of the Cr-N system obtained at $P_N = 3.5 \cdot 10^{-4}$ torr (1 – $U_b = -120$ V and 2 – $U_b = -120$ V, $U_{ip} = -1200$ V) and $P_N = 4.8 \cdot 10^{-3}$ torr (3 – $U_b = -120$ V; 4 – $U_b = -120$ V, $U_{ip} = -1200$ V)

Results of the analysis of the substructural characteristics performed both using the Selyakov-Scherrer equation and in a number of cases by the approximation method [15] are represented in Table 1.

It is seen that at low pressure of a nitrogen atmosphere ($3.5 \cdot 10^{-4}$ torr), when the formation of two main phases – metal Cr(N) with dissolved in the lattice nitrogen atoms and lower nitride Cr_2N – occurs, crystallite size both in the pulse-free mode and with the pulse action is almost the same and is equal to $L \approx (8.5 \dots 9)$ nm for Cr and $L \approx (6.2 \dots 6.7)$ nm for Cr_2N . A lower value of the average crystallite size for CrN is connected with the dispersion of phases in the presence of a dissolved interstitial element.

Table 1 – Phase composition, texture plane and substructural characteristics of the coatings of the Cr-N system obtained at different pressures of a nitrogen atmosphere

| P_N , torr | Phase/ texture plane | $U_b = -120$ V | $U_b = -120$ V, $U_{ip} = -1200$ V |
|---------------------|-------------------------|--|---------------------------------------|
| | | L , nm | L , nm |
| $3.5 \cdot 10^{-4}$ | Cr ₂ N/(111) | 6.15 | 6.76 |
| | Cr(N)/(110) | 8.52 | 8.97 |
| $7.5 \cdot 10^{-4}$ | Cr ₂ N/(300) | 7.47 | 8.88 |
| $1.8 \cdot 10^{-3}$ | CrN/(200) | 5.60 | 6.34 |
| | CrN/(220) | 5.85 | 6.19 |
| $4.8 \cdot 10^{-3}$ | CrN/(200) | 5.78 | 6.49 |
| | CrN/(220) | 6.31 | 6.78 |
| | CrN/(111) | $L = 14.71$ nm $\varepsilon = 0.26$ % | |

Increase in the average crystallite size of the Cr₂N phase to 7.5 nm without the pulse action and to 8.9 nm under the pulse stimulation is observed with increasing pressure to $7.5 \cdot 10^{-4}$ torr.

In the coatings obtained at larger pressure $P_N = 1.8 \cdot 10^{-3}$ torr, for which reflexes only from the crystalline CrN phase are revealed, in the case of the pulse-free stimulation crystallite size along the direction of both types of the textures [100] and [110] is of the order of 5.8 nm; pulse action stimulates the formation of the preferred orientation [110] leading to a slight increase in the average crystallite size in this direction to 6.2-6.3 nm.

Single-phase CrN state is also revealed at the highest pressure $P_N = 4.8 \cdot 10^{-3}$ torr. Average crystallite size for a non-textured fraction in all directions is almost the same and is equal to 5.8 nm and 6.4 nm for the coatings without pulse stimulation and with pulse stimulation, respectively. Appearance of the texture [110] axis during pulse stimulation leads to the increase in the average

crystallite size in this direction to 6.8 nm. In the case of the absence of pulse action under the given conditions, the texture [111] is developed at the average crystallite size along the direction of the texture axis of ≈ 10 nm. The true value of the crystallite size is equal to 15 nm taking into account the influence of the active deformation of 0.26 % on the broadening of diffraction reflexes.

4. CONCLUSIONS

1. Phase composition of the coatings obtained by the vacuum-arc evaporation of a chromium target is changed from the polyphase (Cr(N), Cr₂N, and CrN) to the single-phase CrN in the pressure range from $3.5 \cdot 10^{-4}$ to $4.8 \cdot 10^{-3}$ torr. Formation of the polycrystalline structure occurs at the lowest pressure; and texture with the axis [111] perpendicular to the growth surface becomes determinative for the maximum pressure.

2. Application of an additional high-voltage pulse potential of the value of $U_{ip} = -1200$ V (of the duration of ~ 7 % of the total exposure time) leads at low pressure to enhancement of nitride formation that is exhibited at the pressure of $3.5 \cdot 10^{-4}$ torr in the formation of the Cr₂N phase and at $P_N = 7.5 \cdot 10^{-4}$ torr – in the appearance of the CrN phase.

3. At higher pressure $(1.8...4) \cdot 10^{-3}$ torr application of U_{ip} stimulates the formation of the texture with the axis [110]. Formation of the texture [110] corresponds to the lowest energy of the radiation defect formation at high mobility of atoms stimulated by deposition of high-energy accelerated particles.

4. On the substructural level, transition from the Cr metal phase to nitride at low pressure $P_N = 3.5 \cdot 10^{-4}$ torr leads to the dispersion of crystallites that is manifested in the decrease in the average size from 8.5...9.0 nm to 6.2...6.7 nm.

REFERENCES

- R.L. Boxman, S. Goldsmith, *Surf. Coat. Technol.* **52**, 39 (1992).
- S. Ulrich, C. Ziebert, M. Stuber, E. Nold, H. Holleck, M. Goken, E. Schweitzer, P. Schloßmacher, *Surf. Coat. Technol.* **188**, 331 (2004).
- X.M. Xu, J. Wang, J. An, Y. Zhao, Q.Y. Zhang, *Surf. Coat. Technol.* **201**, 5582 (2007).
- Y.L. Su, S.H. Yao, Z.L. Leu, C.S. Wei, C.T. Wu, *Wear* **213**, 165 (1997).
- X.T. Zung, S. Zhang, C.Q. Sun, Y.C. Liu, *Thin Solid Films* **424**, 99 (2003).
- E. Martinez, J. Romero, A. Lousa, J. Esteve, *Surf. Coat. Technol.* **163-164**, 571 (2003).
- Y.C. Chim, X.Z. Ding, X.T. Zeng, S. Zhang, *Thin Solid Films* **517**, 4845 (2009).
- F.A. Smidt, *Int. Mater. Rev.* **35**, 61 (1990).
- R.M. Bradley, J.M.E. Harper, D.A. Smith, *J. Appl. Phys.* **60**, 4160 (1986).
- J.A. Thornton, *Ann. Rev. Mater. Sci.* **7**, 239 (1977).
- M. Marinov, *Thin Solid Films* **46**, 267 (1977).
- J. Pelleg, L.Z. Zervin, S. Lingo, N. Croitoru, *Thin Solid Films* **197**, 117 (1991).
- G.N. Van Wyk, H.J. Smith, *Instrum. Meth.* **170**, 433 (1980).
- O.V. Sobol', A.A. Andreyev, S.N. Grigor'yev, V.F. Gorban', M.A. Volosova, S.V. Aleshin, V.A. Stolbovoy, *Metallovedeniye i termicheskaya obrabotka metallov* No4, 43 (2012).
- V.M. Beresnev, O.V. Sobol', A.D. Pogrebnyak, P.V. Turbin, S.V. Litovchenko, *Tech. Phys.* **55** No6, 871 (2010).