DOI 10.1007/s11182-023-03056-2
Russian Physics Journal, Vol. 66, No. 11, January, 2024

PHYSICAL AND MECHANICAL PROPERTIES OF CrN/AlN COATING OBTAINED BY VACUUM-ARC DEPOSITION WITH ALTERNATIVE SEPARATION OF HARD SUBSTANCE FLOWS

A. A. Leonov,[1] Yu. A. Denisova,[1] V. V. Denisov,[2] V. M. Savostikov,[1]
M. S. Syrtanov,[2] A. V. Pirozhkov,[2] and A. N. Shmakov[1,3]

UDC 621.793.14

The paper deals with multilayer CrN/AlN *coatings fabricated by the plasma-assisted vacuum-arc deposition onto a* WC–8Co *alloy substrate. The use of a screen for separating alternately* Cr *and* Al *flows, allows to create a multilayer coating structure with* CrN *and* AlN *nanolayers. The X-ray diffraction analysis shows that the structure of obtained coatings consists of* CrN *and* AlN *phases with the face-centered cubic crystal structure. It is found that a 5 rpm rotation speed of the turning table is the best and provides the most appropriate ratio between the thickness of* CrN *and* AlN *layers and the ratio between their phase compositions. This allows minimizing the wear rate intensity of the coatings. The in situ synchrotron X-ray diffraction analysis confirms the presence of* CrN *and* AlN *phases in the temperature range of ~1075 to 1080°C.*

Keywords: vacuum-arc deposition, multilayer coating, XRD analysis, physical and mechanical properties, synchrotron radiation.

INTRODUCTION

More intensive operation of machinery and tools requires the improvement of heat and wear resistance of their working surface by depositing protective and hardening coatings. In this connection, a combination of CrN and AlN compounds in the coating is rather interesting for the production of coatings possessing a high thermal stability in ambient air and low resistance to mechanical wear [1, 2]. Previous research [3, 4] has documented that the hardness and resistance to mechanical wear can be improved *via* the creation of a multilayer architecture of CrN/AlN coatings. In this paper, we explore various approaches to providing the heat resistance and high mechanical and tribological properties of the above-mentioned coating compositions. In the first place, it is assumed that changing the velocity of the sample passage relative to the maximum of the plasma flux distribution of the solid substance (chromium or aluminum), it is possible to change the thickness of deposited layers and, thus, physical and mechanical properties of the obtained coating. In the second place, a shielding screen is applied during the coating deposition, which (at least for a short time!) separates the plasma generated by the dual source.

MATERIALS AND METHODS

The plasma-assisted vacuum-arc deposition was used for multilayer coatings on the upgraded version of NNV6.6-I1 equipped with two electric-arc evaporators with the 80 mm cathode and the additional plasma source

---

[1]Institute of High Current Electronics of the Siberian Branch of the Russian Academy of Sciences, Tomsk, Russia, e-mail: laa-91@yandex.ru; yudenisova81@yandex.ru; denisov@opee.hcei.tsc.ru; svm.53@mail.ru; [2]National Research Tomsk Polytechnic University, Tomsk, Russia, e-mail: maxim-syrtanov@mail.ru; alpir11260@gmail.com; [3]Budker Institute of Nuclear Physics of the Siberian Branch of the Russian Academy of Sciences, Novosibirsk, Russia, e-mail: highres@mail.ru. Original article submitted November 9, 2023.

"PINK" [5, 6]. The discharge circuit consisted a metal screen installed on the turning table at floating potential and crossed the central axis of the vacuum chamber. Electric-arc evaporators with Cr (purity: 99.5%) and Al (purity: 99.8 wt.%) cathodes were installed on lateral sides of the working chamber. The "PINK" source was placed on the door of the vacuum chamber. Internal chamber walls made of stainless steel served as the anode for metal and gas plasma sources. The "PINK" source was used to clean the substrate surface by the ion bombardment, substrate heating, and additional ionization of the gas plasma component, which affected the growing layers, and the metal plasma component. Cylindrical samples of a diameter 10 mm and 7 mm thick made of the WC–8Co alloy were used for the coating deposition. During the deposition process, the substrate holder rotated around the central axis of the vacuum chamber at a 200 mm from it and around its axis. Prior to the experiment, the vacuum chamber was evacuated by a turbomolecular pump to a limit pressure of $2\cdot10^{-2}$ Pa. The working gas argon was fed through the "PINK" source; the working pressure was 0.3 Pa. In igniting the gas discharge and applying –600 V bias potential to the holder, substrates were heated up to ~400°C. After the ionic-bombardment cleaning and chemical activation of the substrate surface, discharges were ignited in electric-arc evaporators, and the coating was deposited onto the substrate. The best current values of electric-arc evaporators were selected in a series of experiments and thus equaled 80 and 30 A for Cr and Al cathodes, respectively. The CrN/AlN coatings were deposited at a 0.3 Pa pressure in a mixture of N_2 and Ar gases taken in the ratio 9 to 1. The deposition time was 120 min. The negative bias voltage was 150 V for all deposition conditions. During the coating deposition with a view to change the thickness of as-deposited layers, the different rotation speed of the turning table was used, *sc*. 3.5, 5, 8 and 12 rpm. The rotation speed values were used for notation of CrN/AlN coatings. The thickness of as-deposited coatings was ~3 μm.

The coating microstructure was investigated on a JEM-2100F (JEOL Ltd., Japan) high-resolution transmission electron microscope (TEM). Thin (100–200 nm) foils were cut from the WC–8Co alloy substrate using a standard procedure and then thinned by a JEOL EM-09100IS Ion Slicer (Japan) with the Ar-ion beam. The coating phase composition was investigated on the XRD-7000S X-ray Diffractometer from Shimadzu. Measurements were conducted using Cu Kα radiation. The analysis of the phase composition was performed using the Crystallographica Search-Match program, PDF4+ database, and PowderCell 2.4. Rietveld program. Nanohardness of multilayer coatings was tested on an NHT-S-AX-000X Nanohardness Tester (CSEM, Switzerland) fitted with a Berkovich three-sided pyramid indenter, at the indentation load increasing from 0 to 20 mN and 1.5 μm/min loading rate, which was then reduced to zero at a frequency of 10 Hz. The NHT-S-AX-000X measured the hardness by Oliver and Pharr method. Pin-on-disk tribology test method was used to study coatings using a profilometer (Tribotechnic, France). The tribological properties at high temperature were examined using the pin-on-disc method. Testing conditions included a 25 mm/s sliding speed, 5 N indentation load, 3 mm wear scar, and 500 m travel, balls of diameter 6 mm used as counter bodies.

The X-ray diffraction (XRD) analysis was conducted for the synchrotron radiation beam of the VEPP-3 storage ring, in Siberian Synchrotron and Terahertz Radiation Centre of the Budker Institute of Nuclear Physics SB RAS, Novosibirsk, Russia. The XRD analysis helped to study the high-temperature resistance and stability of the structure and phase composition of CrN/AlN coatings in the temperature range of 30 to 1300°C. The substrate was heated in the HTK 2000 (Anton Paar) high temperature chamber. XRD patterns were recorded by the position sensitive detector OD-3M-350, and Fityk (1.3.1) program used for the obtained data processing. The process parameters included 0.172 nm wavelength, 10°C/min heating rate, 28–59 degrees Bragg reflection angle.

RESULTS AND DISCUSSION

Figure 1 illustrates the relation between the wear parameter, friction coefficient of CrN/AlN multilayer coatings, and rotation speed of the turning table. The lowest (0.474) coefficient of friction, and the lowest ($0.70\cdot10^{-6}$ $mm^3N^{-1}m^{-1}$) wear parameter are observed at the rotation speed of 5 rpm. Such an improvement of tribological properties of CrN/AlN multilayer coatings with the rotation speed increased from 3.5 to 5 rpm, is probably associated with the lower thickness of CrN and AlN layers. CrN/AlN coatings obtained at higher (8 and 12 rpm) rotation speeds, demonstrate higher values of the friction coefficient of about 0.595 and a higher wear, which exceeds by almost two times the wear of the coating deposited at 5 rpm. The wear parameter and the friction coefficient of CrN/AlN coatings obtained at 8 and 12 rpm, are similar to those of homogeneous $Cr_{1-x}Al_xN$ coatings with the different

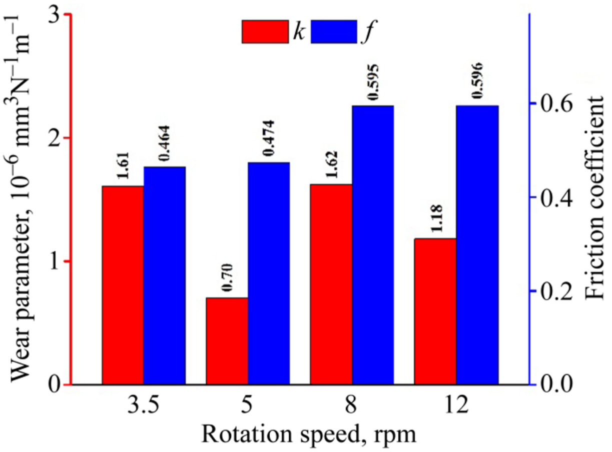

Fig. 1. Relation between the wear parameter *k* and friction coefficient *f* of CrN/AlN multilayer coatings.

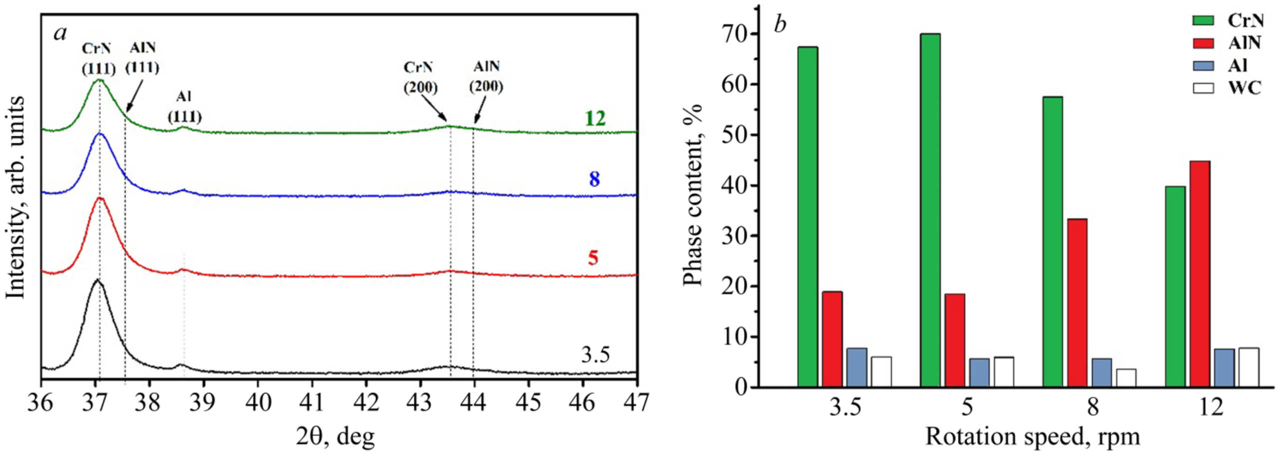

Fig. 2. XRD patterns of CrN/AlN multilayer coatings (*a*), volume fraction of detected phases (*b*).

Al content, as reported in [7, 8]. This suggests that CrN and AlN layers deposited at such rotation speeds, are too thin, and a diffuse interface probably appears between them. The wear parameter usually has the same tendency as compared to the change in the friction coefficient of CrN/AlN coatings (see Fig. 1) [8]. In general, the higher friction coefficient results in the higher wear rate.

In Fig. 2*a*, XRD patterns are obtained for CrN/AlN multilayer coatings. Their structure includes CrN and AlN phases with the face-centered cubic (FCC) crystal structure. Aluminum nitride is stable at normal conditions of the FCC crystal structure. One of the ways to stabilize the AlN cubic structure, is its alloying with titanium or chromium. In this approach, aluminum and chromium are sputtered simultaneously, and then partially mixed. This results in a stabilized cubic structure of aluminum nitride. XRD patterns for all samples demonstrate peaks of superposed CrN and AlN phases. There are also pure Al peaks in all XRD patterns.

The block-diagram in Fig. 2*b*, describes the phase content/rotation speed relation for coatings deposited at different rotation rates of the turning table. One can see that the coating obtained at 5 rpm, consists of 70% CrN, which is maximum, and 18.5% AlN, which is minimum as compared to other coatings. This phase composition probably provides better tribological properties for the coating deposited at 5 rpm, since, as is known, CrN coatings manifest excellent tribological properties [6].

TABLE 1. Nanoindentation Results

Coatings	*H*, GPa	*E*, GPa	*H*/*E*
CrN	21 ± 0.7	281 ± 6	0.07
3.5	29 ± 2	405 ± 21	0.07
5	28 ± 3	356 ± 31	0.08
8	27 ± 1	391 ± 29	0.07
12	31 ± 4	414 ± 39	0.07

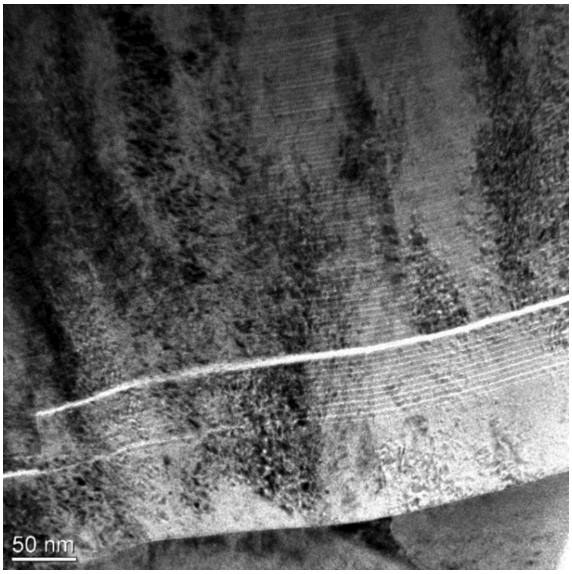

Fig. 3. Cross-sectional TEM image of CrN/AlN coating deposited at 5 rpm.

The cross-sectional TEM image of CrN/AlN coating deposited at 5 rpm, is presented in Fig. 3. The structure of this coating is completely dense, columnar, with alternating nanolayers of CrN (darker color) with the thickness of 3.5 to 4.3 nm, and AlN (lighter color) with 1 or 1.5 nm thickness. As can be seen from Fig. 3, the interface between these nanolayers is well-defined. The spacing between layers is less than 6 nm. This value range provides the best properties for the coating, since the AlN phase has the FCC structure at this layer thickness. Lin *et al*. [9] obtain CrN/AlN coatings with the interlayer spacing of 2.0 to 4.7 nm. Their thickness is more than 30 GPa, and the FCC AlN phase is similar to that of NaCl. In our studies, the nanohardness significantly reduces down to 23–25 GPa with increasing interlayer spacing up to 22.5 nm, where the AlN layer structure is similar to wurtzite.

Table 1 summarizes nanoindentation results, namely: nanohardness *H*, elastic modulus *E*, and *H*/*E* ratio for CrN/AlN and CrN coatings. According to this table, the hardness of the CrN/AlN coating ranges between 27 and 31 GPa, which is higher than that of the CrN coating with the hardness on the order of 21 GPa. The higher hardness of the CrN/AlN coating is probably associated with its multilayer structure, detected by TEM. The ratio *H*/*E* is often used to measure the plastic resistance of the coating. One can see that the highest *H*/*E* ratio belongs to the CrN/AlN coating deposited at 5 rpm, that indicates to its better tribological properties.

Figure 4 presents results of the data array processing, i.e., a series of XRD patterns for the CrN/AlN coating during heating in air. This coating consists of chromium and aluminum nitrides, metallic aluminum in the amount of ~5 to 7%. The unit cell parameters of chromium and aluminum nitrides and metallic aluminum change during heating, indicating to a mutual dissolution of components. This process continues until the temperature of ~725 to 730°C, and then Al peaks disappear, while nitride peaks demonstrate only a shift caused by thermal expansion. CrN and AlN

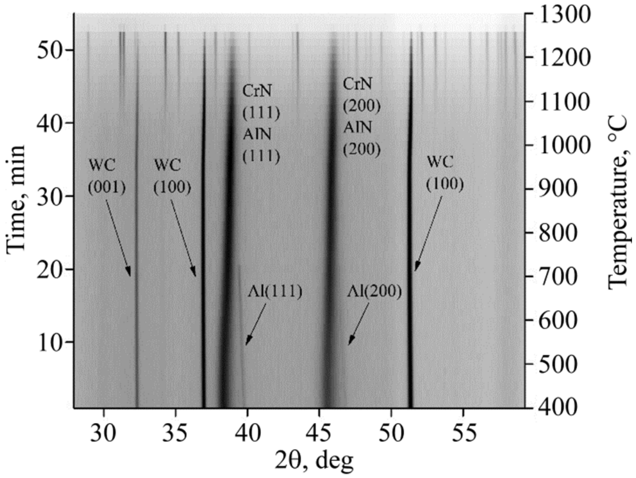

Fig. 4. A series of XRD patterns illustrating the structural changes across the CrN/AlN coating during heating in air up to 1300°C.

phases show their thermal stability up to ~1075 to 1080°C. After that the coating starts to oxidize, and CrN and AlN peaks disappear within ~1255 and 1260°C.

CONCLUSIONS

From the research that has been carried out into mechanical and tribological properties and thermal stability of the CrN/AlN coating, it is possible to conclude that

– the use of a screen for separating alternately Cr and Al flows, provided an effective formation of the multilayer coating structure with CrN and AlN nanolayers;

– the XRD analysis showed the presence of FCC CrN and AlN phases in the obtained coatings;

– a change in the rotation speed of the turning table allowed changing the properties of the CrN/AlN multilayer coating;

– the rotation speed of 5 rpm was the most suitable for the coating deposition. It provided the best ratio between the thickness of CrN and AlN layers and their phase compositions;

– the *in situ* synchrotron X-ray diffraction analysis confirmed the presence of CrN and AlN phases in the temperature range of ~1075 to 1080°C, when the coating was heated up to 1300 °C. After that, the coating started to oxidize. These values indicated to the high thermal resistance of the CrN/AlN coating deposited in described conditions.

COMPLIANCE WITH ETHICAL STANDARDS

Conflicts of interest

The authors declare no conflict of interest.

Funding

Research was financially supported by the Ministry of Science and Higher Education of the Russian Federation (Project No. 075-15-2021-1348, research line 3.1.18).

Financial interests

The authors declare they have no financial interests.

Non-financial interests

None.

REFERENCES

1. K. Bobzin, T. Brogelmann, J. Mayer, A. Aretz, M. R. Iskandar, N. C. Kruppe, and M. Naderi, Appl. Surf. Sci., 569, 151024 (2021); https://doi.org/10.1016/j.apsusc.2021.151024.
2. Z. Chen, D. Holec, M. Bartosik, P. H. Mayrhofer, and Z. Zhang, Acta Mater., **168**, 202 (2019); https://doi.org/10.1016/j.actamat.2019.02.004.
3. F. Ma, J. Li, Z. Zeng, and Y. Gao, Appl. Surf. Sci., **428**, 414 (2018); https://doi.org/10.1016/j.apsusc.2017.09.166.
4. G. S. Kim, S. Y. Lee, J. H. Hahn, and S. Y. Lee, Surf. Coat. Technol., **171**, 95 (2003); https://doi.org/10.1016/S0257-8972(03)00244-5.
5. V. V. Denisov, Y. A. Denisova, E. L. Vardanyan, E. V. Ostroverkhov, A. A. Leonov, and M. V. Savchuk, Russ. Phys. J., **64**, 150 (2021); https://doi.org/10.1007/s11182-021-02310-9.
6. A. A. Leonov, Y. A. Denisova, V. V. Denisov, M. S. Syrtanov, A. N. Shmakov, V. M. Savostikov, and A. D. Teresov, Coatings, **13**, 351 (2023); https://doi.org/10.3390/coatings13020351.
7. J. Lin, J. J. Moore, B. Mishra, M. Pinkas, X. Zhang, and W. D. Sproul, Thin Solid Films, **517**, 5804 (2009); https://doi.org/10.1016/j.tsf.2009.02.136.
8. J. Lin, B. Mishra, J. J. Moore, and W. D. Sproul, Surf. Coat. Technol., **201**, 4334 (2006). https://doi.org/10.1016/j.surfcoat.2006.08.090.
9. J. Lin, J. J. Moore, B. Mishra, M. Pinkas, and W. D. Sproul, Surf. Coat. Technol., **204**, 940 (2009). https://doi.org/10.1016/j.surfcoat.2009.04.013.