Impact wear-resistance of Ti-Cr-B-N coatings produced by pulsed CAE of ceramic target

Ph V Kiryukhantsev-Korneev, K A Kuptsov
National University of Science and Technology ‘MISIS’, 4 Leninsky Prospekt, Moscow 119049, Russia

E-mail: kiruhancev-korneev@yandex.ru

Abstract. Ti–Cr–B–N coatings were successfully deposited using reactive pulsed cathodic arc evaporation (CAE) of ceramic TiCrB target. The influence of the substrate negative bias voltage on the coating impact wear resistance and mechanical properties has been studied. Structural investigations have been carried out using X-ray diffraction analysis, transmission and scanning electron microscopy, glow-discharge optical-emission spectroscopy, and optical profilometry. The coating properties have been estimated by impact tests, scratch-test, and nanoindentation. The obtained results show that the coatings consist of Ti(Cr)N fcc phase with crystallites 1–2 nm in size and amorphous BNx tissue. The coatings obtained at U bias=-250 V demonstrated highest hardness of 24 GPa, whereas samples deposited at U bias=-500V exhibited minimal wear rate (worn area of 12 μm²) in impact conditions. Coatings obtained by pulsed CAE with intensive ion-bombardment possess high adhesion strength higher than 120 N.

1. Introduction

Hard wear resistant coatings for various applications can successfully be deposited by magnetron sputtering of composite targets fabricated using self-propagating high-temperature synthesis (SHS) [1]. Previously, magnetron sputtering have been used for sputtering of the SHS targets in the DC mode [2–5], in the pulsed DC [6-8], RF [9], and HIPIMS [10] modes. There are limited data [11] on preparing coatings by cathodic arc evaporation of SHS targets, although this method has several undoubted advantages. The main advantage of vacuum-arc evaporation, in comparison with magnetron sputtering, is the high energies of particles; dominance of ions in the flow transferred to the substrate; and, accordingly, better coating adhesion [12]. An undesirable feature of arc evaporation is the formation of the drop phase, which degrades coating properties. To exclude drop-phase formation, various techniques can be applied: mechanical separation, electromagnetic filtration, cathode rotation, and pulsed mode of CAE [13–15]. The pulse mode provides more arc spots with a higher motion velocity [15]. The increase in the arc-spot motion velocity reduces the probability of drop-phase formation and leads to a more uniform distribution of the heat flow over the target surface and volume, thus reducing the arising thermal stresses. The latter circumstance is very important for SHS ceramic cathode materials that are sensitive to thermal impacts. The aim of present work was to study coatings obtained by pulsed CAE of SHS targets and analyze the influence of the substrate negative bias voltage on the coating properties including adhesion, and impact wear resistance. The objects of study were Ti–Cr–B–N coatings showed excellent combination of mechanical, tribological properties, thermal stability, wear- and corrosion resistance [16].

2. Experimental part
The TiB–38%Cr4Ti–4%Cr2Ti cathode 18 mm in diameter and 7 mm thick for CAE was fabricated from Ti, Cr, and B powders using SHS force pressing technology. The coatings were deposited using a UVN-2M pumping system and a Sokol 50/20 pulsed-arc evaporator. A scheme and photograph of the evaporator are shown in Fig. 1. The parameters of CAE were fixed on level: ignition frequency 20 Hz, ignition voltage 7 kV, discharge voltage and current 200 V and 1.2 A, respectively, total pressure 0.07 Pa, atmosphere 100% N2, substrate-cathode/anode distance (Ls-k/a) of 20/10 mm. Negative bias voltage (Ubias) was varied between 0 and -500V (Table 1). The typical pulse configuration is shown on Fig. 1.

![Scheme of evaporator](image-a)

![Photograph of process](image-b)

![Pulse configuration](image-c)

**Figure 1** - Pulsed CAE of TiCrB target: scheme of evaporator (a), photo of process (b), and pulse configuration (c)

**Table 1.** Structure and properties of Ti-Cr-B-N coatings.

| №  | U_{bias} (V) | Concentrations (at.%) | D_{111} (nm) | H (Gpa) | E (Gpa) | W (%) | Ra (nm) | S (μm²) |
|----|--------------|-----------------------|--------------|---------|---------|-------|--------|---------|
| 1  | 0            | Ti 39 Cr 13 B 27 N 21 | 1.8          | 22      | 213     | 52    | 24     | 43      |
| 2  | -250         | - - - -             | 1.6          | 24      | 226     | 53    | 21     | 70      |
| 3  | -500         | Ti 38 Cr 13 B 37 N 12 | 1.1          | 21      | 268     | 50    | 19     | 12      |

The substrate materials were Si plates (deposition time of 20 min), Ni foils (20 min), and WC-6%Co discs (1h). Before depositing coatings, the substrates were subjected to ultrasonic treatment in isopropyl alcohol. The element depth profiles were obtained by glow discharge optical emission spectroscopy (GDOES) using a Profiler 2 instrument (Horiba Jobin Yvon, France) [17]. Using these profiles, we calculated depth-averaged elemental concentrations. The coating structures were analyzed by Raman spectroscopy (LabRam Horiba JY spectrometer), transmission and scanning electron microscopy (TEM and SEM) with JEM-200CX Jeol and S-4800 Hitachi microscopes. X-ray diffraction (XRD) analysis was carried out with a Geigerflex Rigaku diffractometer using CoKα radiation. The hardness, modulus of elasticity, and elastic recovery of the coatings were determined at load of 8 mN using a Nano Hardness Tester nanoindenter (CSM Instruments) equipped with a Berkovich indenter. The indentation curves were calculated by the Oliver-Pharr method [18]. Adhesion strength was estimated by means of a scratch tester (CSM Instruments, Switzerland). Impact wear were studied using “ball-on-plate” impact tester (Cemecon, Germany). The coatings deposited onto cemented carbide substrates were subjected to a range of impacts at a constant impact frequency of 50 Hz using a cemented carbide ball with 5-mm diameter. The deformation zone of a sample was cooled by compressed air. Each sample was subjected to tests at 250 N for 10⁵ cycles. The coating roughness and impact cavities were studied using a Wyko 1100NT optical profiler.
3. Results and Discussion
The GDOES analysis showed that all elements were distributed uniformly through the coating thickness. Average concentrations are listed in the Table 1. Results of SEM showed that the coatings possess dense homogeneous structure (Figure 2).

It can be seen that there are no columnar-structure elements that are typical for CAE deposited reference TiN coatings. Particles of crystallized drop phase, which determines the coating roughness, can be seen on the surface. The Raman data revealed, along with the TiN-based phase, boron–nitrogen bonds (peaks in the spectra at ~1380 and ~1580 cm$^{-1}$), which can be explained by the presence of amorphous phase and/or a small amount of hexagonal phase (with a composition similar to BN) in the coatings [19-20]. Note that according to the Raman study the flat regions and droplets have the same structure (Fig. 2). The roughness measurements for Ti–Cr–B–N coatings showed that the $Ra$ parameter decreases from 24 to 19 nm with an increase in the bias from 0 to −500 V. Note that obtained results are close or slightly better compare to the results for Ti–B–N CAE coatings obtained before [19] and possess $Ra=22–56$ nm. Thus, Ti–Cr–B–N coatings have a satisfactory roughness. Decreasing of $Ra$ parameter with $U_{bias}$ can be explained by intensification of surface ion bombardment, sputtering/evaporation of deposited droplets, and decreasing of the droplet concentration.

Selected area diffraction patterns (Fig. 2) showed that fcc phase based on titanium nitride is main component of coatings 1-3. Comparison of dark-field images obtained by TEM showed that the crystallite size decreased from 1.8 to 1.1 nm when $U_{bias}$ was raised from 0 up to −500V. According to the XRD results there are strongly broadened low-intensity peaks in the coating-diffraction patterns between the positions of the (111) and (200) lines of titanium nitride, as well as narrow high-intensity lines from the silicon substrate at ~38°. The mean crystallite size ($D_{111}$) estimated by Scherrer formula decreases from 1.8 to 1.1 nm with an increase in the bias magnitude from 0 to −500 V, which can be explained by the more intense ion bombardment of the growing coating, which leads to a higher surface energy, stronger crystallite imperfection, and larger number of crystallization centers.

Scratch-test of the Ti-Cr-B-N coatings deposited by pulsed CAE method with intensive preliminary ion etching showed that samples has excellent adhesion to the cemented carbide substrate (Fig. 3).
Microscopic examination of scar regions has not revealed the formation of any cracks and serious delaminations of the coatings up to maximal load of 120 N. Some fragments of materials around deformation zone can be attributed to the wear of the coating or substrate during test. Note that Ti-Cr-B-N coatings deposited by magnetron sputtering demonstrated critical load of failure in range 30-40 N [21]. Nanoindentation experiments showed that coating 2 has the highest hardness, H=24 GPa and elastic recovery, W=53%, whereas coating 3 exhibited maximal elastic modulus, E=268 GPa (Table 1). The internal stresses, crystallite size and the volume fraction of amorphous phase are known to strongly affect the mechanical properties of nanocomposite coatings. Previously, the hardness values for magnetron-sputtered Ti–Cr–B–N coatings obtained using a similar SHS target were found to be ~17 GPa for coatings with a crystallite size of 1–2 nm and high amorphous-phase content [21]. Optical 2D and 3D images of impact cavities obtained after the impact-tests at 250N for 10⁵ cycles are shown in Fig. 4.

The Ti-Cr-B-N coatings obtained at Ubias=−500V exhibited the smallest deformation zone size and impact wear area (S) (Table 1) compared to the coatings deposited with smaller bias. The high wear rate of coating 2 can be due to its high hardness. In the process of testing the microparticles break away from the coating and play role of abrasive. Similar data were obtained in the work dedicated to the Cr-B-N coatings [22]. It should also be mentioned that although the plasticity index, H/E and resistance of a coating to plastic deformation H³/E², were proposed to be a reliable indicator of wear resistance in a coating [23], it does not explain the difference in behavior of the coatings during impact testing. The 3 coatings exhibited minimal H/E=0.08 and also minimal H³/E² = 0.13 GPa. Perhaps
internal stresses, crack resistance, crystallite size, and volume of amorphous phase are more significant parameters for this type of test.

4. Conclusion
The nanocomposite nc-TiCrN/a-BN coatings were obtained by pulsed CAE technology at substrate bias voltages of 0, -250, and -500 V. The coatings demonstrated dense, non-porous structure, relative low concentration of the condensed droplet phase and low roughness (Ra=19-24 nm), hardness between 21 and 24 GPa, high critical load of adhesive failure (>120 N), good impact wear resistance (worn areas between 12 and 70 μm²). The combination of high hardness, adhesion strength, and wear resistance makes Ti–Cr–B–N CAE deposited coatings promising candidates for protective coatings to be used in various tribological applications.

Acknowledgments
We thank M.Ya. Bychkova for scratch-test. This work was carried out with financial support from the Ministry of Education and Science of the Russian Federation in the framework of state assignment No.11.7172.2017/8.9.

References
[1] Levashov E A, Mukasyan A S, Rogachev A S and Shtansky D V 2017 International Materials Reviews 62 203
[2] Shtansky D V, Lyasotsky I V, D'yakonova N B, Kiryukhantsev-Korneev F V, Kulinich S A, Levashov E A and Moore J J 2004 Surface and Coatings Technology 182 204
[3] Kiryukhantsev-Korneev Ph V, Iatsyuk I V, Shvindina N V, Levashov E A, Shtansky D V 2017 Corrosion Science 123 319
[4] Paternoster C, Fabrizi A, Cecchini R, Spigarelli S, Kiryukhantsev-Korneev Ph V, Sheveyko A 2008 Surface and Coatings Technology 203 736
[5] Shtansky D V, Sheveyko A N, Sorokin D I, Lev L C, Mavrin B N, Kiryukhantsev-Korneev Ph V 2008 Surface and Coatings Technology 202 5953
[6] Audronis M, Lelyand A, Matthews A, Kiryukhantsev-Korneev F V, Shtansky D V, Levashov E A 2007 Plasma Processes and Polymers 4 687
[7] Lin J, Mishra B, Moore J J, Pinkas M and Sproul W D 2008 Surface and Coatings Technology 203 588
[8] F. V. Kiryukhantsev-Korneev, K. A. Kuptsov, A. N. Sheveiko, E. A. Levashov, D. V. Shtansky 2013 Russian Journal of Non-Ferrous Metals 54 330
[9] Zhong D, Moore J J, Mishra B M, Ohno T, Levashov E A and Disam J 2003 Surface and Coatings Technology 163-164 50
[10] Kiryukhantsev-Korneev Ph V, Horwat D, Pierson J F and Levashov E A 2014 Technical Physics Letters 40 614
[11] Werner Z., Stanislawski J, Piekoszewski J, Levashov E A and Szymczyk W 2003 Vacuum 70 263
[12] Kiryukhantsev-Korneev F V, Shirmanov N A, Sheveiko A N, Levashov E A, Petrzhek M I, Shtanskii D V 2010 Russian Engineering Research 30 909
[13] Martin P J and Bendavid A 2001 Thin Solid Films 394 1
[14] Leng Y X Chen J Y, Wang J Wan G J, Sun H Yang P, Huang N 2006 Surface and Coatings Technology 201 157.
[15] Witke T, Schuelke T, Schultrich B, Siemroth P, Vetter J 2000 Surface and Coatings Technology 126 81
[16] Kiryukhantsev-Korneev F V, Sheveiko A N, Komarov V A, Blanter M S, Skryleva E A, Shirmanov N A, Levashov E A and Shtansky D V 2011 Russian Journal of Non-Ferrous Metals 52 311
[17] Kiryukhantsev-Korneev Ph V 2012 *Protection of Metals & Physical Chemistry of Surfaces* **48** 585

[18] Pharr G M, Oliver W C, Brotzen F R 1992 *Journal of materials research* **7** 613

[19] Ben el Mekki M, Djouadi M A, Guiot E, Mortet V, Pascallon J, Stambouli V, Bouchier D, Mestres N and Nouet G 1999 *Surface and Coatings Technology* **116–119** 93.

[20] Ben el Mekki M, Mestres N and Pascual J 2006 *Surface and Coatings Technology* **201** 2553

[21] Kiryukhantsev-Korneev F V, Petrzhik M I, Sheveiko A N, Levashov E A and Shtanskii D V 2007 *The Physics of Metals and Metallography* **104** 167

[22] Kiryukhantsev-Korneev Ph V, Pierson J. F Bychkova M. Y., Manakova O. S, Levashov E. A. Shtansky D. V. 2016 *Tribology Letters* **63**(3):44

[23] Leyland A and Matthews A 2000 *Wear* **246** 1