

Structure and properties of hard nanostructured coatings in Cr-B-N system

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The CrB₂ thin coatings are of interest because of their high hardness, wear- and corrosion resistance [1,2]. Incorporation of nitrogen in transition metal-boron systems (TiB₂, ZrB₂ etc.) often leads to enhancing of chemical, mechanical and tribological characteristics [3,4]. The objective of the present study is the investigation of structure and properties of Cr-B-N coatings.

The CrB₂ targets were synthesized from exothermal powder mixtures by means of self-propagating high-temperature synthesis [5]. The Cr-B-N coatings were obtained using DC magnetron sputtering of CrB₂ target in an argon atmosphere or in a gaseous mixtures Ar+N₂ (Table 1). The total pressure was maintained at 0.2 Pa. The diameter of the targets was 12.5 cm and the distance from the target to substrate was 9 cm. During deposition, the applied bias voltage was kept constant at -250 V and the substrate temperature was controlled at 250-300°C. Coatings were deposited on single crystal Si (100), Ni foil, and cemented carbide substrates for various times to obtain 1.0-2.5 μm thick coatings.

The structure, phase, and chemical composition of coatings were studied by means of transmission and scanning electron microscopy (TEM and SEM), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and electron probe microanalysis (EPMA). To evaluate the oxidation resistance and thermal stability, the samples were annealed at 500, 700 and 900°C in air for 1 hour. The elemental depth profiles for oxidized coatings were obtained by second ion mass-spectrometry (SIMS). Adhesion (critical load Lc₂), hardness (H), Young's modulus (E) friction coefficient (f) and wear rate (Vw) were evaluated by means of scratch-tester, nanohardness tester, and pin-on-disk tribometer (CSM Instruments). The electrochemical tests of the Cr-B-N coatings were carried out in 5N H₂SO₄ using three-electrode cell and VoltaLab 50 potentiostat (Radiometr analytical).

Chemical composition of coatings obtained by EPMA is present in the Table 1.

Table 1. Chemical composition and properties of Cr-B-N coatings

No	%N ₂	Concentration, at %			H, GPa	E, GPa	H/E	W, %	Lc ₂ , N	f	Vw, mm ³ N ⁻¹ m ⁻¹	i _p , mAcm ⁻²
		Cr	B	N								
1	0	30.9	69.1	0	29	297	0.0976	59	45	-	-	2.61
2	10	30.6	62.8	6.6	36	273	0.1319	72	>90	0.79	6.9·10 ⁻⁶	3.09
3	15	30.1	57.2	12.7	23	220	0.1045	68	70	0.77	3.6·10 ⁻⁶	0.59
4	25	29.5	54.7	15.8	19	177	0.1073	68	>90	0.76	3.9·10 ⁻⁶	0.076
5	85	-	-	-	15	151	0.0993	66	-	0.78	5.1·10 ⁻⁶	-

The nitrogen concentration in coatings increased from 0 to 15.8 at % when the nitrogen partial pressure was raised from 0 to 25%. Note that B/Cr ratio in coatings was equal to 2.2.-1.9 and did not significantly change with nitrogen partial pressure. Carbon and oxygen were also detected in an amount of 2.0-2.5 at %. Their occurrence can be explained by the presence of impurities in the target and/or in the residual gas within the chamber.

According to the Cr2p and B1s XPS spectra, CrB₂ was the main phase in non-reactive coating No. 1. In contrast, the CrB₂ and BN phases were detected in all reactive deposited coatings Nos. 2-4. The volume fraction of BN phase increased with nitrogen concentration. Other phases, such as CrB, Cr₂B, CrN and Cr₂N [6,7] were not detected in the Cr2p, B1s and N1s spectra of Cr-B-N coatings Nos. 2-4.

The structural characterization using XRD and selected area electron diffraction patterns identified all the Cr-B-(N) coatings except No. 5 as having a hexagonal close-packed AlB₂-type structure and no additional phases were detected (Fig. 1). The coatings deposited in Ar and at lowest nitrogen partial pressure of 10% were highly textured with (001) axis normal to the substrate surface. The (001) preferred orientation became less pronounced when nitrogen partial pressure was further raised. According to dark-field TEM images, the average crystallite size decreased from 15-17 nm for non-reactive coatings to 5 and 3 nm for the coatings deposited in gaseous mixtures of Ar+N₂ with 10% and 15-25% of nitrogen (Fig. 1). It may be result from CrB₂-crystals growth interruption by thin amorphous layers, probably based on BN. The morphology of coatings changed from dense-columnar (coatings No. 1) to the globular (Nos. 2-4) when the nitrogen was added in the working gas. The XRD spectra for coating No. 5 had two broad peaks with low intensity near position of cubic face-centered CrN. The very fine crystallites of CrN phase, 1-1.5 nm in size, were embedded in the BN phase. The TEM data for the No. 5 are presented in Fig.1.

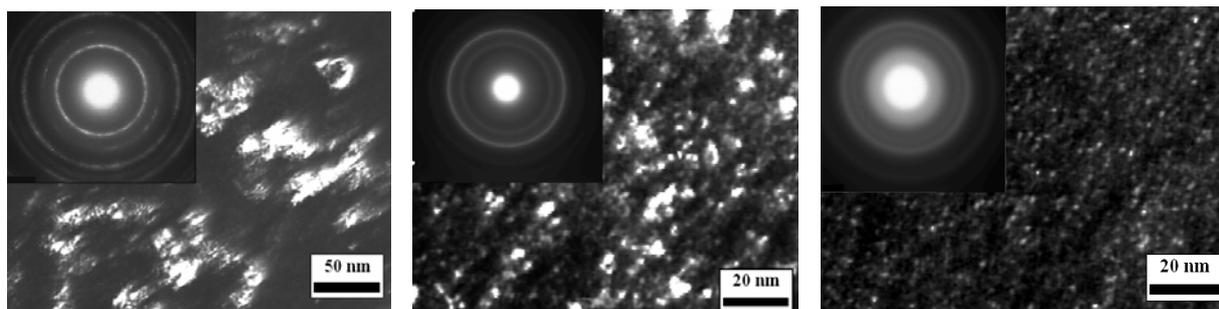


Fig. 1. Dark-field TEM-images and selected area electron diffraction patterns of coatings No. 1, No. 2, and No. 5 (from left to right).

The values of hardness, Young's modulus and elastic recovery are present in the Table 1. Coatings deposited on Si substrate were evaluated at the normal load of 4 mN. It can be seen that the hardness versus nitrogen concentration has an extreme character. The maximum value 36 GPa was obtained for coatings No. 3 with 6.6 at % of nitrogen. When the nitrogen concentration was further raised, the hardness significantly decreased. The better mechanical properties of sample No. 3 may be attributed with maximal level of the compressive stress about 2.2 GPa. For other coatings the lower values in the range of 0.2-1.7 GPa were recorded. The combination of stoichiometric composition of crystalline CrB₂ phase and optimal volume fraction of amorphous BN phase in the coating No. 3 can also positively affect the hardness [8,9]. Note that coating No.3 showed highest value of elastic recovery up to 72%. The Young's modulus decreased from ~300 down to ~180 GPa when nitrogen concentration were raised from 0 to 15.8 at %. It is a result of increasing of soft a-BN phase concentration in coatings.

The coating No. 1 showed a good adhesion to the cemented carbide substrate. The first delamination was observed at the load 45-50 N. The coatings Nos. 2-4 demonstrated resistance to failure up to 70-90 N and even higher. This difference may be related with higher elastic

properties of Cr-B-N coatings (Table 1). Note that cracks at the borders of the scar were only observed in the coatings with low nitrogen concentration. Thus nitrogen alloying enhanced the fracture toughness of relatively brittle chromium diboride coatings.

The tribological tests were performed with normal load 5 N and linear speed 10 cm/s, using 3-mm 100Cr6 ball. The non-reactive coatings wore up to substrate at the first 10 m of distance because high fragility, whereas all coatings with nitrogen showed low wear rate within the range of $(3-7) \cdot 10^{-6} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$. No correlation between hardness and wear resistance were observed. In contrast, the H/E ratio [10, 11] can be used to predict tribological behavior (Table 1). The 3D images of the wear tracks are presented in Fig. 2. The friction coefficient of Cr-B-N coatings was within the range of 0.76-0.79 during the whole sliding distance of 130 m.

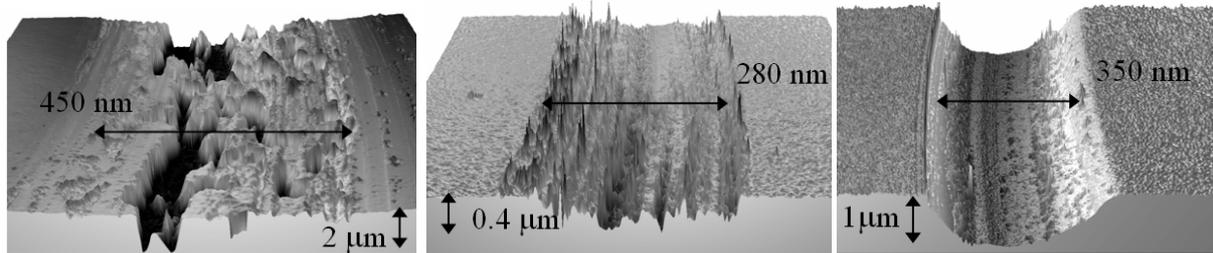


Fig. 2. The 3D images of the 2 μm thick coatings No. 1, No. 2, and No. 5 (from left to right) after tribological tests

The oxidation depth for annealed coatings was obtained from SIMS element depth profiles. Because thickness of the oxide layers for Cr-B and Cr-B-N coatings treated at 500°C

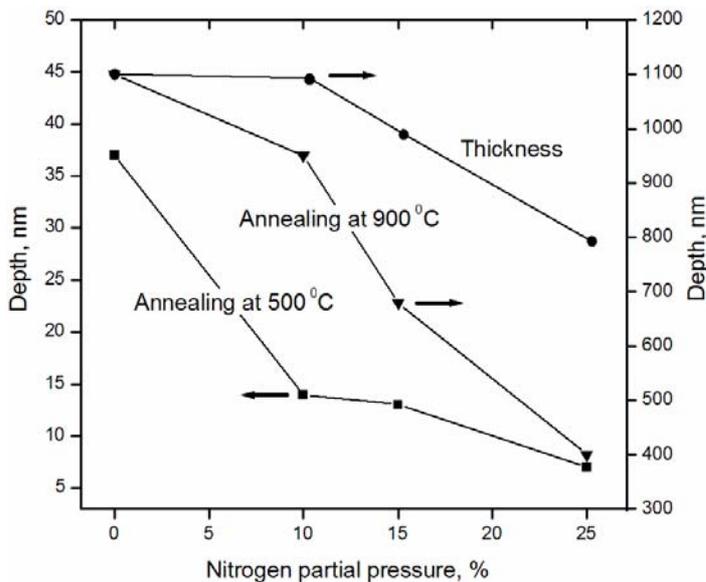


Fig. 3. The oxidation depth and coating thickness vs. nitrogen partial pressure

was less than 50 nm, second neutral mass-spectrometry was used to obtain the higher depth resolution. The dependence of the oxidation depth and coating thickness vs. nitrogen partial pressure, are shown on the Fig. 3. Oxidation rate of nitrogen-doped coatings Nos. 2-4 at 500°C was 2.5-5 times lower than that of Cr-B coatings. The positive effect of nitrogen can be attributed to the formation of amorphous a-BN phase. It is known that diffusion of non-metal atoms (oxygen) through the disordered areas is complicate to compare the crystalline structure [12, 13]. Dense non-columnar structure with minimal volume of the voids can be responsible for high oxidation resistance. The Cr-B coatings were completely

oxidized after annealing at 900°C, whereas coatings No. 2, No. 3, and No. 4 were partly oxidized with the oxidation depth of 86%, 68% and 50% of the coating thickness, respectively. The XRD-spectra of the coatings Nos. 3-4 annealed at 700-900°C showed peaks from CrB₂ and Cr₃O phases. The formation of protective chromium oxide and chromium borate top-layers during heating can play important role for the enhancing of oxidation resistance of boronitride coatings [14, 15]. Note that negative effect of nitrogen on the oxidation resistance of Cr-B-N coatings was reported [16].

The electrochemical tests were performed for the ~ 1 μm thick coatings deposited on the Si substrate. Prior to tests, samples were masked with a lacquer leaving 0.2 cm² for interaction with the electrolyte. The free corrosion potentials were recorded after stabilization period for 1 hour. The 1N H₂SO₄, 5N H₂SO₄ and 1N HCl solutions were used as environments. The maximal difference between coatings was obtained in 5N H₂SO₄. The results obtained show that non-reactive coatings and coatings Nos. 2 and 3 with low nitrogen content showed similar negative free corrosion potential -230 mV. In contrast, coatings with 15.8 at % of nitrogen demonstrated positive value close to 250 mV. Potentiodynamic polarization measurements were performed over the electrode potential from -0.5 to 1.3 V with respect to the free corrosion potential with a scan rate of 1 mV/s. The passivation current densities (*i_p*) are listed in the Table 1. All Cr-B-N coatings exclude No. 2 had higher corrosion resistance (lower values of *i_p*) than Cr-B. The poor corrosion resistance of Cr-B-N coating No. 2 can be related with maximal level of compressive stresses in the coating.

The results obtained showed that the Cr-B-N coatings possess mechanical, tribological and anti-corrosion characteristics significantly higher than those of chromium diboride coatings. The advanced combination of properties makes Cr-B-N coatings promising candidate for protective coatings to be used in different environments.

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