INFLUENCE OF BIAS VOLTAGE ON COMPOSITION AND TRIBOLOGICAL PROPERTIES Ti-Cr-N COATINGS FORMED BY ION-PLASMA DEPOSITION

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ABSTRACT

Ti-Cr-N coatings were formed on St3 steel by cathodic arc vapor deposition while combining titanium or chromium plasma flows in a residual nitrogen atmosphere. Elemental and phase composition of the coatings were studied using Auger electron spectroscopy (AES) and X-ray diffraction (XRD). Coatings are solid solution on the basis of chromium and titanium mononitrides. It is found that an increase in bias voltage leads to relative rise of titanium concentration and to decrease of chromium concentration. With the values of bias voltage less than 120 V coatings grow with (200) preferred orientation. It is established that Ti-rich coatings ($Ti_{31}Cr_{20}N_{49}$ and $Ti_{33}Cr_{17}N_{50}$) have low steady-state friction coefficient, while the Cr-rich coatings ($Ti_{17}Cr_{35}N_{48}$) has high steady-state friction coefficient.

Key words: Ti-Cr-N coating; ion-plasma deposition; bias voltage; elemental composition; phase composition; tribological properties.

INTRODUCTION

Thin hard coatings of nitrides of transitional metals fabricated by the cathodic arc vapor deposition (CAVD) are now widely used for cutting tool and wear applications due to their specific mechanical properties, such as high oxidation resistance, hardness, adhesion to the substrate, wear and corrosion resistance. Ti-Cr-N coatings are particularly suitable as anti-wear coatings to increase lifetime of cutting tools working in extremely difficult conditions [1-3]. Ternary transition metal nitride coatings provide wide range of structures providing control of mechanical and tribological properties [4-7].

The aim of this paper is to investigate the influence of the process parameters on changes of the elemental, phase composition and tribological properties of Ti-Cr-N coatings, formed by ion-plasma deposition.

EXPERIMENTAL

Carbon steel St3 (weight %: 0,2 C; 0,2 Si; 0,5 Mn) was used as a substrate

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material. Specimens were made in discs of 20 mm in diameter and 5 mm thick. The coatings were formed by CAVD method with combining plasma flows of titanium and chromium in a residual nitrogen atmosphere [3, 8].

Prior to the deposition, substrate surface was cleaned and heated by chromium ion bombardment for 1 min with the substrate bias $V_{bias}= -1$ kV, arc current of Cr cathode was 100 A, vacuum in the chamber was 10^{-3} Pa.

The formation of all coatings was accomplished with the following regimes: the nitrogen pressure in vacuum chamber was about 10^{-1} Pa; arc currents of chromium and titanium cathodes were 100 A, deposition time was 10 min. Ti-Cr-N coatings were deposited by varying bias voltage in the range from $V_{bias}= -30$ to $V_{bias}= -230$ V that made it possible to change energy characteristics of the deposition process. Average thickness of the prepared coatings was about 3 μm.

Chemical composition of the formed coatings was analyzed using an Auger electron spectroscopy (AES). The distribution of elements was determined by AES with step-by-step sputtering of the samples surface layer by argon ions with the energy of 3 keV. Phase composition was investigated by X-ray diffraction with Cu K_α radiation.

Tribological behavior of the coatings was studied comparatively with back-and-forth motion spherical indentor VK8 (hard alloy WC – 92 w.%, Co – 8 w.%) at a rate of 4 mm/s in the atmospheric environment. Load on the indentor was 1 N. Surface morphology and sliding tracks were studied by scanning electron microscopy (SEM) combined with energy dispersive X-ray analysis (EDXA).

RESULTS AND DISCUSSION

Figure 1 summarizes results of AES analysis of the elemental composition of Ti-Cr-N coatings obtained under different conditions of deposition. It is revealed that metallic components are uniformly distributed in the depth in all formed coatings. From these results it is apparent that bias voltage between $V_{bias}= -30$ and -230 V exerts a significant influence on the coating composition (*table 1*). Thus, relative titanium concentration rises and the chromium concentration decreases with an increase ofs bias voltage. In all cases, nitrogen concentration remains constant and is about ~ 50 at.%. For the simplicity coatings were termed as $Ti_{17}Cr_{35}N_{48}$, $Ti_{31}Cr_{20}N_{49}$ and $Ti_{33}Cr_{17}N_{50}$.

Table 1 – Deposition conditions and composition of Ti-Cr-N coatings

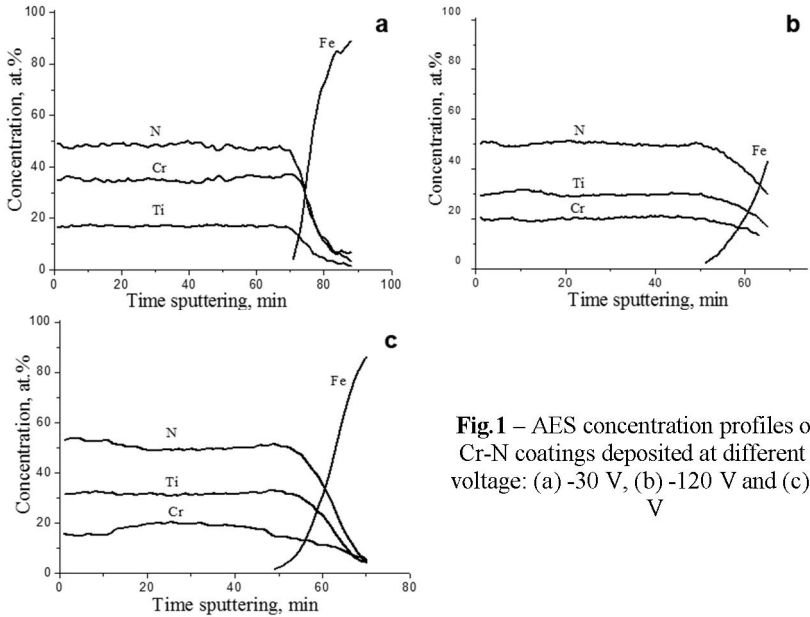| Samples	Deposition of coatings, U_{bias}, V	Concentration, at.%			Designation
		Ti	Cr	N	
1	-30	17	35	48	$Ti_{17}Cr_{35}N_{48}$
2	-120	31	20	49	$Ti_{31}Cr_{20}N_{49}$
3	-230	33	17	50	$Ti_{33}Cr_{17}N_{50}$

Fig.1 – AES concentration profiles of Ti-Cr-N coatings deposited at different bias voltage: (a) -30 V, (b) -120 V and (c) -230 V

It should be noted that bias voltage influences not only element, but also phase composition of the coatings. *Figure 2* presents a fragment of the XRD pattern of Ti-Cr-N coatings, deposited on steel substrate. Basic diffraction peak of the coatings is located between the peaks titanium nitrides TiN (fcc) and chromium nitride CrN (fcc) that indicates the formation of solid solution with the B1 NaCl crystal structure. Solid solution is formed on the basis of crystal lattice of nitride of titanium.
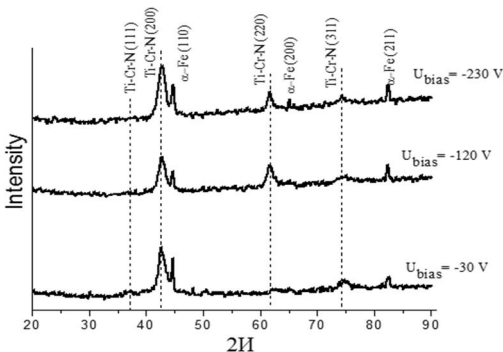

Fig.2 – X-Ray diffraction patterns Ti-Cr-N coatings deposited at different bias voltage

This is caused by the fact that heat of formation of titanium nitride (ΔH_{TiN} = - 336,8 kJ/(g·atom)) is considerably higher than that for chromium nitride (ΔH_{CrN} = - 118,0 kJ/(g·atom)) [9]. During the condensation of substance from the plasma the atoms of chromium replace

titanium atoms in the lattice of titanium nitride.

It is established, that all the coatings possess (200) preferential orientation. However, bias voltage influenced preferred grain orientation. It can be seen that for Ti-Cr-N coating deposited at $V_{bias}= -30$ V, a combination of (200) and (311) orientations was found; while for $V_{bias}= -120$ and -230 V, an additional (220) orientation was observed.

This is connected with the influence of energy characteristics of plasma flow and possible additional temperature rise of the base layer, to the processes of growth and to the subsequent increase in the coatings. As the bias voltage increases the energy of the bombarding ions rises, in turn: one can modify coating growth conditions (and thus, its structure), lead to resputtering of the growing coating, change residual stresses and, hence, coatings properties [10-12].
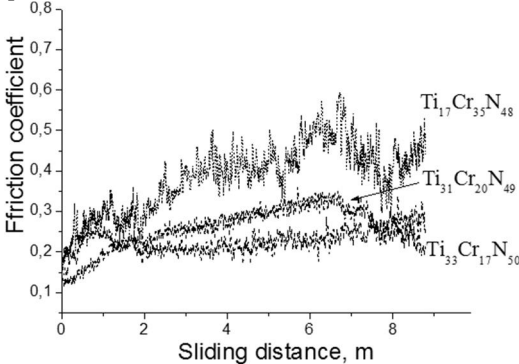

Fig.3 – Friction coefficient of the Ti-Cr-N coatings

Figure 3 shows results of tribological tests. On the initial stages of the wear track sliding process is affected by Ti and Cr microdroplets. But as the sliding continued the microdroplets were freed from the surface and swept away by sliding ball. It is established, that the Ti-rich coatings (Ti$_{31}$Cr$_{20}$N$_{49}$ and Ti$_{33}$Cr$_{17}$N$_{50}$) have low steady-state friction ($\sim$ 0.2) coefficient, while the Cr-rich coatings (Ti$_{17}$Cr$_{35}$N$_{48}$) has high steady-state friction ($\sim$ 0.4) coefficient. The width of sliding tracks on the face surface decreased with an increase of bias voltage (Figure 4).
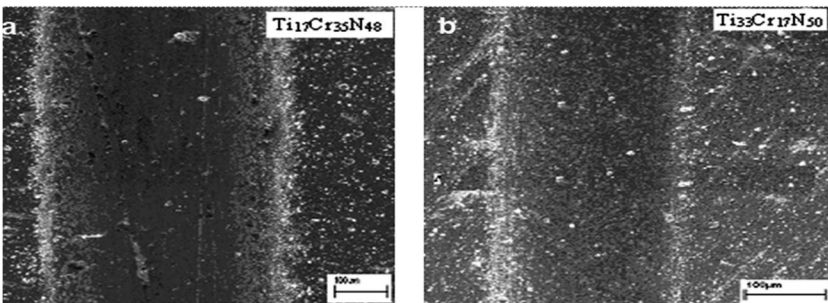

Fig.4 – Sliding track of the Cr-rich (a) and Ti-rich (b) coatings

The possible reasons for this is the decrease of roughness [13] and density of microdroplets on the surface of coatings, and also decrease of grain size, contributing to the enhanced mechanical strength.

CONCLUSIONS

Ti-Cr-N coatings were formed by condensation from a plasma phase in vacuum with ion bombardment of the sample surface by titanium and chromium plasma flows in a residual nitrogen atmosphere. The formed coatings exhibited solid solutions with B1 NaCl crystal structure and preferred orientation of growth (200). It is found, that relative concentration of titanium rises from 17 at.% to 33 at.% and the concentration of chromium decreases from 35 at.% to 17 at.% with an increase in the bias voltage. It is shown that steady-state friction coefficient of the Ti-rich coatings less in 2 times as compared with steady-state friction coefficient of the Cr-rich coatings.

REFERENCES

[1] D.B. Lee, M.H. Kim, Y.C.Lee, S.C. Kwon, Surface & Coatings Technology, 2001, Vol. 141, P. 232-239.

[2] J.J. Nainaparampil, J.S. Zabinski, A. Korenyi-Both, Thin Solid Films, 1998, Vol. 333, P. 88-94.

[3] V.V. Uglov, V.M. Anischik, V.V. Khodasevichet al., Vacuum, 2007, Vol. 81, P. 1345-1347.

[4] J. Bujak, J. Walkowicz, J. Kusiński, Surface & Coatings Technology, 2004, Vol. 180-181, P. 150-157.

[5] V.M. Anischik, V.V. Uglov, S.V. Zlotski, P. Konarski, M. Cwil, V.A. Ukhov, Vacuum, 2005, Vol. 78, P. 545-550.

[6] *A.D. Pogrebnjak, M.M. Danilionok, V.V. Uglov et al.,* Vacuum, 2009, Vol. 83, Suppl. 1, P. S235-S239.

[7] *A.D. Pogrebnjak, Yu.A. Kravchenko, S.B. Kislitsyn et al.* Surface and Coatings Technology, 2006, Vol. 201, № 6, P. 2621-2632.

[8] *V.V. Uglov,* V.M. Anischik, .V.V. Khodasevich et al. Surface & Coatings Technology, 2004, Vol. 180 –181, P.519.

[9] M.I. Goldshtan, S.V. Gratchev, V.G. Veksler, Special steels. 1985; 408 p.

[10] X.T. Zeng, S. Zhang, C.Q. Sun, Y.C. Lui, Thin Solid Films, 2003, Vol. 424, P. 99-102.

[11] V.N. Zhitomirsky, I. Grimberg, L. Rapoport et al. Surface & Coatings Technology, 2000, Vol. 133-134, P. 114-120.

[12] V.V. Uglov, V.M. Anischik, S.V. Zlotski et al. Surface & Coatings Technology, 2005, Vol. 200, P. 178-181.

[13] J.H. Hsieh, W.H. Zhang, C. Li, C.Q. Sun, Surface & Coatings Technology, 2001, Vol. 146-147, P. 331-337.