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An analysis of macroparticle-related defects on CrCN and CrN coatings in dependence of the substrate bias voltage☆

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ABSTRACT

Chromium nitride coatings with and without a carbon content being assigned as CrCN and CrN were prepared by cathodic arc evaporation. The effect of negative substrate bias voltages (10–300 V) on the microstructure, phase composition and morphology of the coating surface was studied. X-ray diffraction data show that almost all coatings crystallized in the cubic structure with (111) and (200) diffraction lines appearing only for low negative bias voltage and a (220) diffraction line being present for the coatings deposited at higher negative bias voltages. For CrN coatings obtained at −300 V a hexagonal structure was also observed. In case of CrCN coatings the (220) diffraction line shows much higher intensity than in case of CrN coatings and was significantly broadened. On the surface of the coatings a large number of macroparticles of different size was observed. An increase of bias voltage causes a reduction of the areal density of macroparticles and a decrease of the mean surface roughness Ra.

1. Introduction

Hard coatings of transition metal nitrides deposited by PVD techniques have found widespread applications. Because of their high hardness, good chemical and wear resistance they are widely used in various industrial applications. Chromium nitride coatings exhibit higher oxidation resistance compared to other nitride coatings, and show good wear resistance under difficult tribological conditions such as high temperature, speed and pressure [1]. Many authors [2–6] describe the influence of carbon in Chromium nitride, i.e. in CrCN-systems, indicating a change in hardness, adhesion, stress, oxidation resistance, and friction coefficient.

One of the major disadvantages of the cathodic arc evaporation technique is a large quantity of macroparticles on the surface of the coating. The macroparticles, emitted from the cathode material, adhere to the substrate and roughen the surface of the coatings.

The bias voltage is one of the most important parameters influencing the mechanical properties of PVD coatings. Huang et al. [7] observed a significant reduction of the number of macroparticles as a result of negative substrate biasing.

Although there have been many papers in the literature studying the effect of technological parameters on the physical, mechanical, structural and tribological properties of CrCN coatings, no study has been performed, to our knowledge, where the effect of bias voltage on properties of such coatings was conducted.

This paper contains the analysis of microstructure, phase composition and morphology of CrCN and CrN coatings deposited on HSS steel substrates (HS 6-5-2) with cathodic arc evaporation at various negative substrate bias voltages (−10 V to −300 V).

2. Experimental details

2.1. Deposition

The coatings were deposited in a multi-source PVD system using cathodic arc evaporation on HS 6-5-2 steel substrates. The cathode was pure chromium. Hardened and annealed steel substrates of 32 mm in diameter and 3 mm thick were mechanically polished to a mean roughness Ra of about 0.02 μm. The samples were chemically degreased and ultrasonically cleaned in a hot alkaline bath for 10 min and dried in warm air. The substrates were placed on a rotational holder about 18 cm away from the chromium cathode. After the system was evacuated to the base pressure of 1 mPa it was filled with argon to about 0.5 Pa. For further cleaning, to remove the surface oxide layer, the substrates were sputter etched using chromium Cr^+ and argon (Ar^+) ion bombardment with a bias

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voltage of −600 V for 20 min. A chromium adhesion layer of about 0.1 μm was first deposited onto the substrates. The CrCN coatings were deposited at a fixed nitrogen partial pressure of 1.8 Pa controlled by a Baratron type capacity gauge. The deposition temperature was 300 °C and a negative substrate bias voltage in the range of 10–300 V was applied. Acetylene was added at a flow rate of 10 sccm, controlled by an MKS 100 mass flow controller.

2.2. Characterization

Structural determination by X-ray diffraction was done with Co Kα radiation. The surface morphology was studied with a scanning electron microscope SEM (JEOL JSM 5500LV).

The roughness of the coatings was determined with a Hommel Werke T8000 profilometer. To assess the surface density of macroparticles a Nikon Eclipse MK200 microscope was used. All images were taken at the same magnification (400×), the same contrast, sharpness and threshold of sensitivity. The software of the microscope acquires automatically the data for the quantitative and dimensional analysis of macroparticles.

3. Results and discussion

From an increase of the bias-controlled energy of the ions impinging onto the growing coating a denser and more perfect structure can be expected. Simultaneously for a high nitrogen pressure the number of macroparticles emitted from the chromium cathode might be increased.

3.1. Phase structure analysis

The X-ray diffraction patterns of CrN in Fig. 1 exhibit the presence of the cubic phase of CrN. The Cr_2N hexagonal phase was also recorded at a bias voltage of −300 V. This phase coexists with the CrN cubic phase. A similar effect was observed also by other authors [8,9]. The increase in substrate bias voltage does not cause [8], or causes only slightly an increase of the metal-to-nitrogen ratio in the chemical composition of coatings [1,10,11] and a reduction of Cr–N bonds [12].

The relative intensity of diffraction lines changes significantly with the bias voltage. CrN (111) and (200) diffraction lines exist only for coatings deposited at a bias of −10 V. The intensity of the (220) diffraction lines of CrN increases with the negative bias voltage. In Fig. 1 diffraction lines of iron from the substrates are also presented.

The diffraction lines are shifted towards lower angles compared to the standard data. This may be caused by residual stress, which is the sum of tensile stress generated at the grain boundaries, compressive stress caused by the ion bombardment, and thermal stress arising from different thermal expansion coefficients of the coating and the substrate [2,3,13].

With increasing negative bias voltage the energy of particles moving on the growing surface increases also. Due to higher atom mobility the texture of the coatings changes from a (111)-texture for −10 V of bias voltage to (220) with increasing bias voltage. The disappearance of the (111)- texture could be also caused by a lower strain energy corresponding to lower residual stress, which is generally observed for CrN when compared with TiN coatings [14].

Similar effects can be observed in Fig. 2 for the CrCN coatings. The effect of preferred (220)- orientation is greater than for the CrN- coatings (see Fig. 1). This is evidenced by the higher Cr (220)-intensity compared to the (110) iron diffraction line as a standard. It should be noted that the thickness of the CrN and CrCN coatings is identical and amounts to 2.2 ± 0.2 μm. A major difference in the diffraction patterns of CrN and CrCN coatings is the absence of Cr_2N hexagonal phase in the latter.

Despite the relatively high concentration of carbon in the CrCN coatings (about 10 at.%) no diffraction lines of chromium-carbon compounds were found. (Fig. 2). This may be associated with the relatively low deposition temperature of 300 °C. The low temperature favors the formation of small crystallites, which in the X-ray measurements do not appear due to a low intensity of corresponding diffraction lines. It may, however, also be associated with the formation of a 3-phase system with the carbon atoms at interstitial positions. The observed small shift of the (220)-diffraction line for CrCN layers (Fig. 2) towards lower angles with respect to the data for CrN layers (Fig. 1) can be related to an increase of the lattice parameters.

The broad diffraction (220)- lines for CrCN and also for CrN indicate the formation of small crystallites and/or the occurrence of internal stress in the coatings. Crystallite sizes determined from the Scherrer equation [15] are approximately 6–8 nm and are similar to those reported by Gautier and Machet [12].

3.2. Morphology and macroparticle statistics

Macroparticles are connected with micro-flaws on the surface leading to a coating failure during tribological stressing. The arc process offers the opportunity of an effective substrate pretreatment.

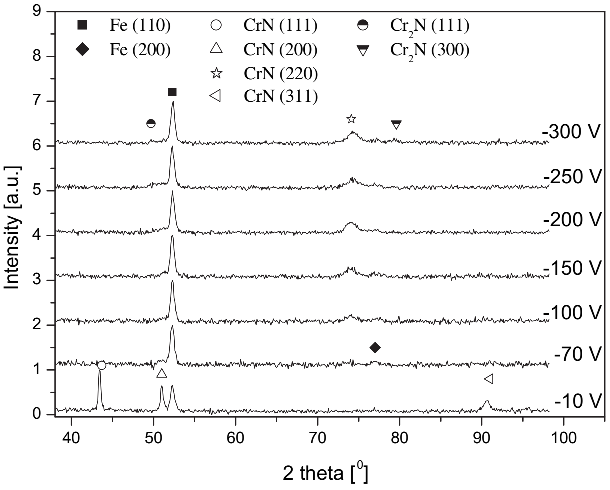

Fig. 1. X-ray diffraction patterns of arc-evaporated CrN coatings.

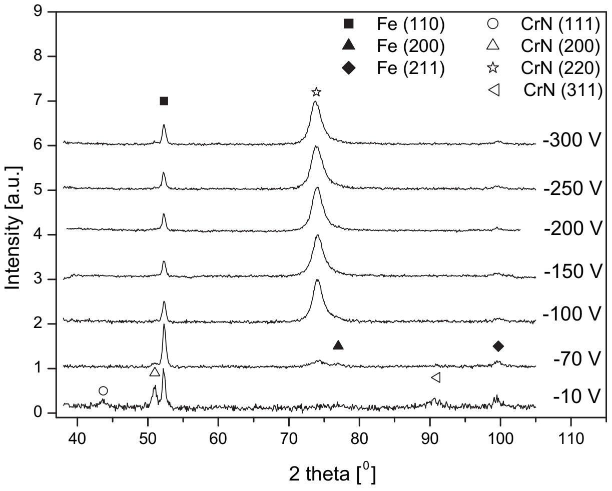

Fig. 2. X-ray diffraction patterns of arc-evaporated CrCN coatings.