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Structure and properties of CrN/DLC coating deposited by PVD ARC-cathodes and PACVD technology

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ABSTRACT

Purpose: The main aim of the this research was the investigation of the microstructure and the mechanical properties of the CrN/DLC coating deposited by hybrid PVD/PACVD process onto the X40CrMoV5-1 hot work tool steel substrate.

Design/methodology/approach: The microstructure of the investigated coating was observed on the scanning electron microscopy and transmission electron microscopy. Tests of the coatings' adhesion to the substrate material were made using the scratch test. A friction coefficient and the wear of coatings were determined in a test according to the ball-on-disk method.

Findings: It was found that the microstructure of the CrN layer consisted of fine crystallites, while their average size fitted about 10 nm. The low-friction DLC show an amorphous character. The coating demonstrated a satisfactory adhesion to the substrate. The values of the critical load LC1 and LC2 of investigation coating account for, respectively, 9 and 39 N. In sliding dry friction conditions, after the break-in time, the friction coefficient for the investigated elements is set in the range between 0.03-0.06. The investigated coatings reveals high wear resistance.

Practical implications: Economically efficient process improvement, increased production efficiency and quality and products reliability through increased durability and unfailing operation time of tools for plastic formation of non-ferrous metals and improved usable properties shall guarantee measurable economic effects to the manufacturers and users of the products. Moreover, it will enhance their competitiveness both on the domestic and overseas markets.

Originality/value: The Author's original approach was the development of a double-layer coating within one process. Such coating consists of the internal hard PVD layer providing the appropriate hardness, strength, low thermal conductivity and restricting the impact of external factors on the wear process and the external low-friction layer providing good tribological properties.

Keywords: Thin & thick coatings; Microstructure; Mechanical properties

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

Surface engineering is one of the most growing area of research because of the high industrial demands for friction control and wear resistance. Protective hard coatings for tools, machine elements and engineering components based on thin transition metal nitrides and/or carbides films possess excellent properties like high hardness and good wear resistance [1-4].

One of the most effective coatings of this type is the CrN coating. CrN coatings have been developed for high-temperature wear applications, such as cutting tools or die casting molds due to their unique mechanical properties and oxidation resistance. CrN coating is one of the most common hard coatings used nowadays. It has been documented that CrN coatings exhibit ow thermal conductivity (12 W/mK), high microhardness (15-25 GPa), good corrosion and wear resistance [5-9].

Thin films deposited by arc evaporation and sputtering methods are widely used in industrial applications. Cathode arc evaporation is the mostly preferred deposition technique owing to its high ionization degree, high deposition rates and its industrial scaling up [10-11].

Diamond-like carbon (DLC) played a very significant role in the reduction of friction resistances, particularly under technically dry friction conditions. Their beneficial tribological properties are mainly related to the slide phenomena taking place in the transitional layer, functioning as a solid lubricant, produced in the friction contact zone as the consequence of the graphitization and DLC coating oxidation. The sp^3/sp^2 atomic carbon ratio in DLC film is strongly related to the quality of DLC films [12-15].

The purpose of this paper is to examine the microstructure, mechanical and tribological properties of coating system CrN+DLC deposited by PVD-Arc cathodes and PACVD technique on the X40CrMoV5-1 hot work tool steel substrate.

2. Investigation methodology

A material for the research consisted of specimens dimensioned ϕ30×5 mm made of hot-work X40CrMoV5-1 tool steel deposited with hard nanocrystalline CrN and low-friction DLC layers produced with the PVD and CVD technique. Prior to the coatings production process, the specimens were ground and polished to obtain the roughness of Ra≤0.03 µm, and then washed in organic solvents and alkali detergent solutions, including the use of ultrasound aid. The so prepared specimens were placed into a work chamber of a coating deposition device.

The production process of hybrid two-layer coatings of the CrN hard nitride layer - low-friction layer DLC type was performed with a π80 and π300+DLC unit by PLATIT.

The fractographic tests of coatings were made on transverse fractures in a scanning electron microscope SUPRA 35 by ZEISS, fitted with the EDS chemical composition analysis technique.

Diffraction investigations and coating structure investigations were conducted using a scanning-electron microscope (S/TEM) Titan 80-300 FEI. Observations were carried out within energy range of 80-300 kV in the classical model (TEM) with a spatial resolution below 0.10 nm and in the beam surface-scanning mode (STEM) with spatial resolution of up to 0.14 nm. Microscope tests were performed on thin lamellas dimensioned about 20×8 µm that were next thinned to the final thickness of about 50-70 nm. Sampling was made on the cross-section of layers with an FIB Quanta 3D 200i device.

The Raman spectra were obtained from DLC layer by Raman scattering technique. The Raman spectra were taken on Renishaw inVia Reflex Raman microscope with λ=514 nm line of 10 mW power output. The data were collected with a 10 s data point acquisition time in the spectral region of 100-3200 cm^{-1}. The Raman spectra obtained were adjusted with Gaussian distribution curves.

Layers' surface topography tests analysis of the tested coatings were determined based on the measurements performed with an atomic force microscope (AFM) XE-100 by Park System.

The adhesion of the coatings to the substrate material was evaluated with a scratch test used commonly for coatings produced in physical vapour deposition processes. The tests were made using a Revetest device by CSM using the following test conditions: pressing force range of 0-100 N; load increase rate (dL/dt) - 100 N/min; indenter movement rate (dx/dt) - 10 mm/min; acoustic emission detector sensitivity - 1.2.

The character of the damage formed was assessed based on observations with an MEF 4A microscope by Leica.

A friction coefficient and the wear of coatings was determined in a test according to the ball-on-disk method. The tests were undertaken at room temperature with a T-01M device by ITE Radom under the following conditions: slide rate - 0.2 m/s (192 rpm); normal load - 19.62 N; friction radius - 10 mm; counter-specimen - an Al_2O_3 ball with 10 mm diameter; wear track - 1,000 m; ambient temperature - 23°C (±1°C); relative humidity - 30% (±5%); and at temperature increased with a high-temperature tribometer by CSM Instruments with the following conditions of the experiment: slide rate - 0.2 m/s (192 RPM); normal load - 5 N; wear radius - 5 mm; counter-specimen - an Al_2O_3 ball with 6 mm diameter; wear track - 500 m; ambient temperature - 400°C (±5°C).The test were performed in compliance with ASTM G99-05 and ASTM G133-05. The wear tracks of the coatings were viewed with a confocal laser scanning microscope CLSM 5 Exciter by Zeiss with a light source of a 25 mW diode laser emitting radiation with a wavelength of 405 nm.

3. Discussion of results

The coating presents a compact structure, without any visible delaminations or defects (Fig. 1). The morphology of the fracture of coating is characterized by a dense microstructure. The fracture surface of the steel sample was examined and the deposited coating shows a sharp transition zone between the substrate and the coating. The thickness of the CrN/DLC coating in this experiment is approximately 1.3 µm.

Observations of surface topography for the analysed coatings using atomic force microscopy (AFM) demonstrate that the observed characteristic columns endings located on surface, forming appropriate coatings, have a shape of reversed pyramids, cones, polyhedrons or craters (Fig. 2).

Tests were carried out using the transmission electron microscope, in order to determine the microstructure and size of crystallites in the layers produced and to examine the character of transition zones between the substrate and the coating, as well as between the individual layers in the coatings. The size and shape of grains in the deposited layers was determined using the dark field technique and based on electron diffractions obtained signifying an amorphous or nanocrystalline microstructure of the analysed layers. The results of the tests obtained using the transmission electron microscopy confirmed the amorphous character of a low-friction DLC layer. The electron diffraction patterns obtained have shown the considerable broadening of diffraction rings (Fig. 3).

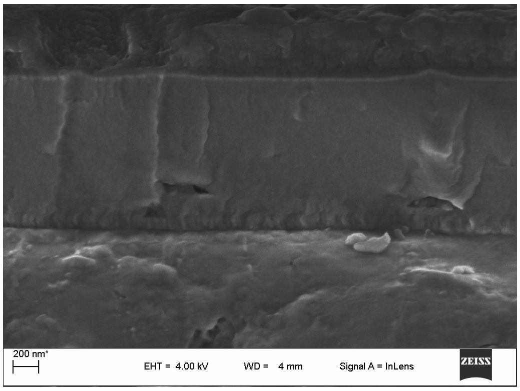

Fig. 1. Fracture image of CrN/DLC coating deposited onto the X40CrMoV5-1 steel substrate

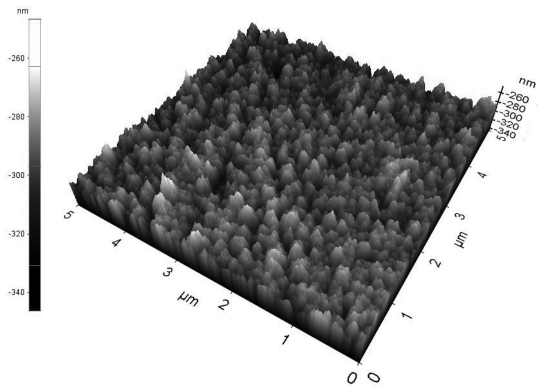

Fig. 2. Image of the CrN/DLC coating surface (AFM)

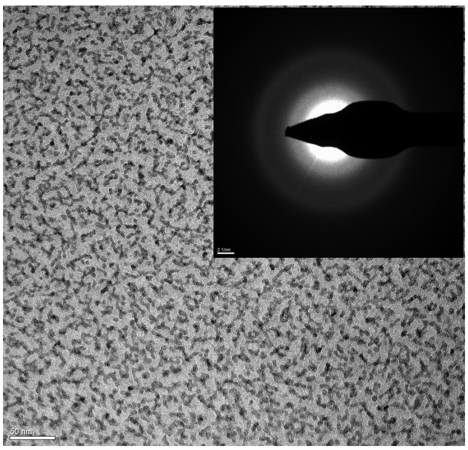

Fig. 3. Microstructure of the DLC layer with corresponding SAED pattern

It was found by examining thin lamellas from the cross section of CrN layer produced by physical vapour deposition technique that the layer features a compact structure with high homogeneity and a grain size about 10 nm (Fig. 4).

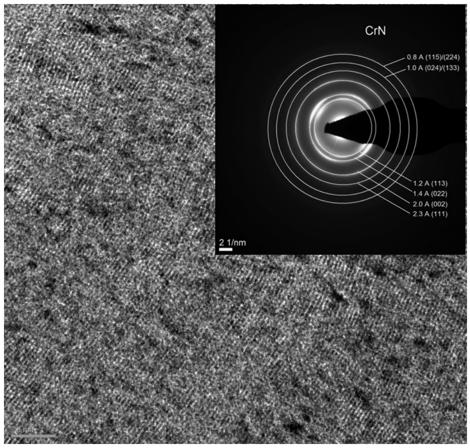

Fig. 4. Microstructure of the CrN layer with corresponding SAED pattern

It can be concluded already based on TEM images in the bright field that the layers have a nanocrystalline structure. Observations in the dark field and the diffraction images made for increasingly smaller areas confirm a nanocrystalline structure of the examined CrN layers.

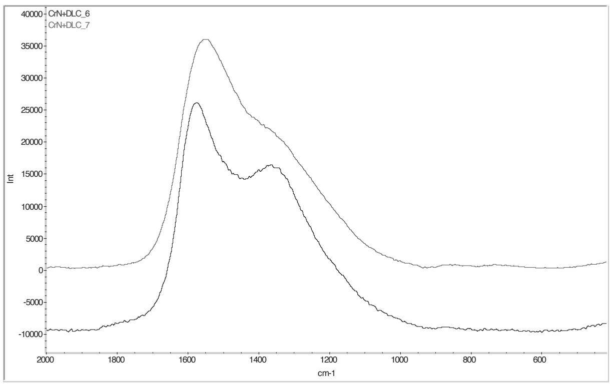

Fig. 5. Raman spectrum of low-friction DLC layer

Moreover, to fully identify the structure of a DLC layer produced by PACVD method, tests were carried out using a Raman spectrometer. Raman spectroscopy is a very useful method in diagnosing different carbon phases and also allows determining clearly the fraction of carbon phases according to the line D and G. A monocrystalline phase of graphite is characterised by an intensive reflex occurring for the dislocation of 1580 cm^{-1}. Diamond features almost a 100% fraction of sp^3 bonds and a narrow band occurring for 1332 cm^{-1}. Intermediate phases, such as DLC or amorphous carbon, are forming sp^2 bonds and are represented by broad D bands (1345-1360 cm^{-1}) and G bands (1500-1580 cm^{-1}). The visible on Fig. 5 double band is typical for an amorphous carbon DLC layer (with sp^2-type bonds prevalent) which also confirms the amorphous character of the DLC layer. The spectrum of the DLC layer is strong. At various points, there are different proportions of G and D bands.

Confocal analysis was performed in the DLC layer into two selected points (Fig. 6). With such thin layer is indicated in the Z axis mapping with very small step. Due to the limited amount of time selected bigger step - 1 µm.

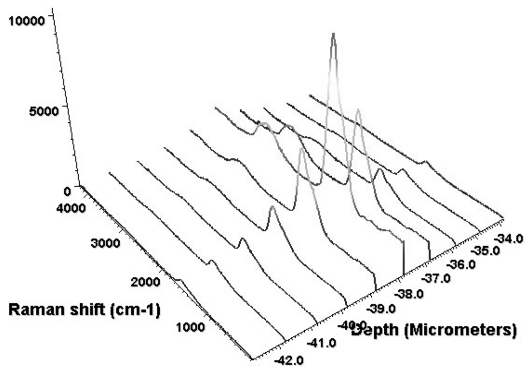

Fig. 6. Waterfall display of the depth profile of DLC layer

The critical load values were determined using the scratch method with the linearly increasing load („scratch test"), characterizing adherence of the investigated coating to the steel substrate (Fig. 7). The investigated coating shows relatively low values of critical load. First failure occurs at very low values (~ 9 N). The second critical load values L_{C2} occurs at 39 N.

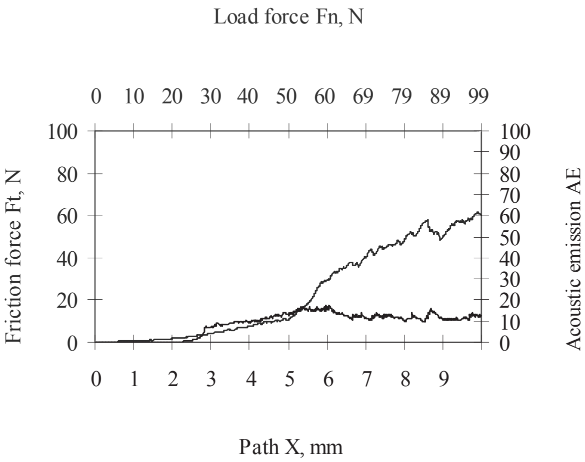

Fig. 7. Diagram of dependence between acoustic emission (AE) and friction force Ft for CrN/DLC coating

The first symptoms of damage of the coating examined are conformal or tensile microcracking indicating cohesive failure within the investigated coatings, as a result of substrate deformation (Figs. 8, 9). Occasionally, there are some small chippings on the scratch edges.

An abrasive wear resistance test in dry slide friction conditions with the ball-on-disk method at room temperature was performed to determine the tribological properties of the tested coatings deposited on a hot-work X40CrMoV5-1 tool steel substrate. Fig. 10 illustrates the diagrams of changes in a dry friction coefficient µ obtained during tests of wear in relation to an Al_2O_3 counterspecimen at the temperature of 20°C for a wear track of 1000 m.

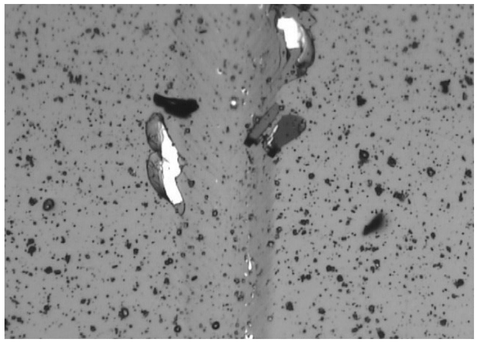

Fig. 8. Scratch failure pictures of the CrN/DLC coating at L_{C1}

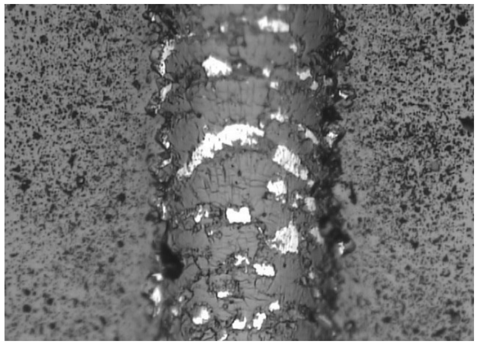

Fig. 9. Scratch failure pictures of the CrN/DLC coating at L_{C2}

The registered friction coefficient for the examined combinations stabilises within 0.03-0.06 (Fig. 10). The CrN/DLC coating and counterspecimens examined exhibit high tribological properties. The values of the coating K_c and counterspecimen K_b wear coefficients were recorded at the level of 10^{-9} mm^3/Nm.

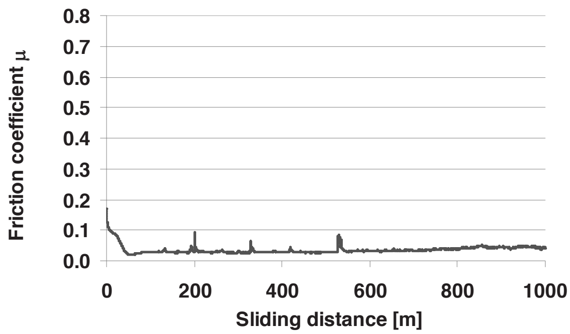

Fig. 10. Relationship between the friction coefficient and wear track obtained based on a wear resistance tests with the ball-on-disk method for the CrN/DLC coating analysed at the temperature of 20°C

Fig. 11 illustrates the diagram of changes in the dry friction coefficient μ obtained during the tests of wear in relation to a Al_2O_3 counterspecimen at the temperature of 400°C for a wear track of 500 m for a load of 5 N. The CrN/DLC coating shows low value of the K_c coating and K_b specimen wear indicators what confirms its high wear resistance at elevated temperature.

The appropriate formation of the structure and properties of wear resistant coatings, their fabrication conditions and material properties must be optimised. Essential for the actual improvement in the quality of different coating systems is high hardness, adequate state of stresses and a possibly lowest friction coefficient. The impact of temperature on the substrate material is limited by a low heat conductivity factor of coatings fabricated with the physical vapour deposition method.

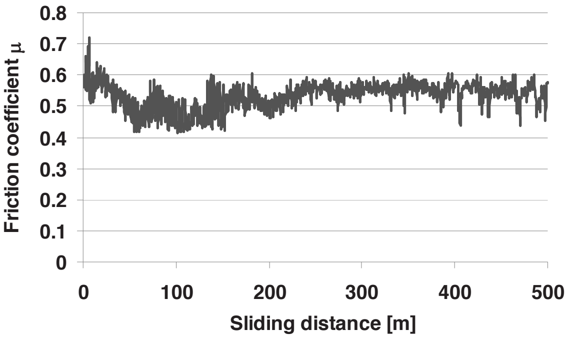

Fig. 11. Relationship between the friction coefficient and the wear track obtained based on a wear resistance test with the ball-on-disk method for the CrN/DLC coating analysed at the temperature of 400°C

4. Summary

Basing on the investigation results the following conclusions were arrived at:

- the CrN+DLC coating was deposited successfully on X40CrMoV5-1 hot work tool steel substrate;
- the TEM investigation indicates that the CrN film has fine crystallites which size is about10 nm;
- under the technically dry friction conditions, the friction coefficient is within the range 0.03-0.06;
- the Raman spectra of the DLC layer reveal two broad bands, typically observed in diamond-like carbon coatings.

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