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Structural investigation and wear resistance of CrAlSiN+DLC coating obtained by hybrid PVD/PACVD process

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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 CrAlSiN+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 high resolution 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 nanocrystalline CrAlSiN layer consisted of fine crystallites, while their average size fitted within the range of 5-10 nm. The low-friction DLC show an amorphous character. The coating demonstrated a good adhesion to the substrate. The values of the critical load L_{C1} and L_{C2} of investigation coating account for, respectively, 36 and 76 N. In sliding dry friction conditions, after the break-in time, the friction coefficient for the investigated elements is set in the range between 0.03-0.05. 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; Nanocrystalline coatings; Microstructure; Mechanical properties

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MATERIALS MANUFACTURING AND PROCESSING

1. Introduction

From tool users prospective, a tool's resistance to damages is most important apart from durability. For several decades, tool material designers have been trying to develop and produce tool material of maximum possible wear resistance characteristics in working conditions. Various attempts were made to find at least a partial solution of the issue by applying thermal-chemical treatment, deposition PVD and CVD coatings as well as laser surface treatment [1-5].

Progress in the manufacture and improvement of service life of tools used in modern industries is mainly achieved because the techniques of depositing thin coatings made of hard ceramic materials resistant to wear are becoming more and more widespread. A wide selection of the currently available types of coatings and deposition technologies derives from a growing demand, in the recent years, for the state-of-art material surface modification and protection methods. From among a myriad of techniques enhancing the strength of materials, CVD (Chemical Vapour Deposition) and PVD (Physical Vapour Deposition) methods are playing an important role in industrial practise [6-9].

As products working in heavy duty conditions are commonly used, it is necessary to intensify research efforts into selection of an appropriate material, production technology and deposition of wear resistant coatings onto them. Nanostructural design of hard coatings has attracted increasing interest in modern development for wear-resistance applications [10-12].

DLC layers exhibit particularly advantageous tribological properties. In general, coatings produced with various methods carry such a term in the literature, as well as those with differentiated chemical and phase composition representing a mixture of amorphous and fine-crystalline carbon with sp^1 hybridisation (linear), sp^2 (trigonal) typical for graphite and sp^3 (tetragonal) typical for diamond. Carbon atoms with sp^1 hybridisation occur only in small amounts, whereas a ratio of sp^3/sp^2 phase fraction is determining the properties and is one of the criteria of carbon coatings' classification. A low friction coefficient and good electrical conductivity is ensured for coatings by sp^2 phase, whereas sp^3 phase fraction is decisive for high hardness, resistance to tribological wear and chemical volume [13-15].

The purpose of this paper is to examine the microstructure, mechanical properties and corrosion resistance of nanocrystalline and gradient coatings deposited by PVD technique on the X40CrMoV5-1 (1.2344) hot work tool steel substrate.

2. Investigation methodology

The production process of hybrid double-layer coatings was performed continuously with a π300 device by PLATIT fitted with LARC (Lateral Rotating Cathodes) cathodes and CERC (Central Rotating Cathode) cathode in a single technological process. In the first stage, hard nanocrystalline CrAlSiN layers were produced with a PVD technique with the arc method. To obtain the high adhesion of coatings, the substrate surface was ion-etched and a chromium-based metallic transition layer was applied. In the second stage, low-friction DLC layers were produced after decreasing the temperature with the PACVD method. To obtain the high adhesion of a low-friction layer, a chromium- and/or titanium based metallic transition layer was applied with the arc method, and next a DLC a-C:H:Si and a-C:H layer with the PACVD method. The coatings were deposited on the X40CrMoV5-1 hot work tool steel substrate.

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, equipped with an electron field gun XFEG with a Schottky emitter with increased brightness, an energy dispersion spectrometer EDS, an external energy filter for imaging EFTEM and for spectroscopy EELS, a system of three BF/ADF/HAADF detectors for scanning work mode. 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.

Tests using a Raman spectrometer Jobin-Yvon (T64000) were made to estimate the ratio of sp^2 and sp^3 bonds in the DLC layers produced. The source of excitation in the spectrometer was laser light with the wave length of 514.5 nm, and a detector was a cooled CCD camera with the resolution of at least 2 cm^{-1}. A laser beam was focussed on a specimen through a ×100 lens. The Raman spectra obtained were adjusted with Gaussian distribution curves.

Layers' surface topography tests**,** a fractional and multifraction 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%).

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 fractographic tests made with the electron scanning microscope (Fig. 1) allow to assert that the tested coatings, depending on the applied system of layers, indicate a double-layer structure consisting of a hard nitride layer and a low-friction layer. It was also found that a chromium-based transition layer exists well bound with a substrate that was fabricated to improve the coatings' adhesion to a hot-work tool steel substrate. The individual layers are deposited uniformly and tightly adhere to each other and to the substrate material. Morphology of the surface of fractures in the tested coatings is characterized by a compact structure.

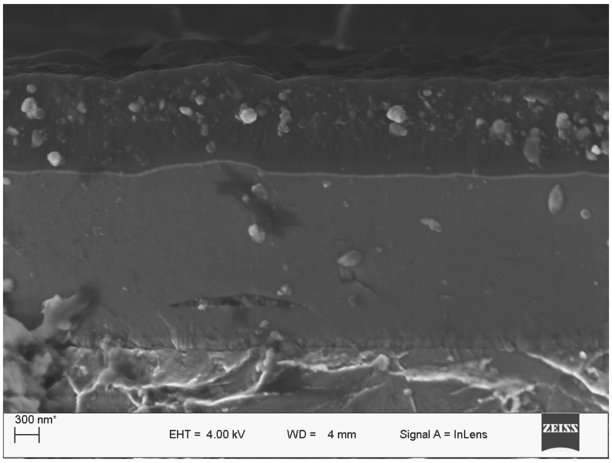

Fig. 1. Fracture image of CrAlSiN/DLC coating deposited onto the X40CrMoV5-1 steel substrate

The observations of the analyzed coatings' surface topography using the atomic force microscopy (AFM) method revealed a varied surface topography of nitride and low-friction layers produced on the surface of hot-work tool steel.

Two types of morphology can be differentiated according to the type of layers. The first one occurs in the case of nitride layer produced by Physical Vapour Deposition with the arc method and is characterized by the existence of single droplet-shaped microparticles. The other one, though, exists for a low-friction DLC layer produced by Plasma-Assisted Chemical Vapour Deposition and is characterized by a high inhomogeneity relating to multiple droplet-shaped or nearly ball-shaped particles existing on the surface (Fig. 2).

Tests were carried out, using the high-resolution transmission electron microscope, in order to determine the structure 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 were determined using the dark field technique and based on electron diffractions obtained signifying an amorphous or nanocrystalline structure 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).

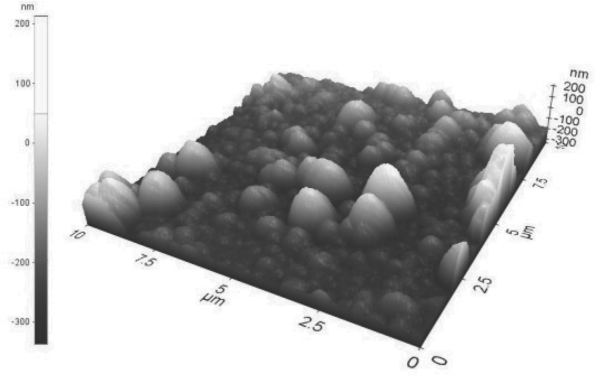

Fig. 2. CrAlSiN+DLC coating fracture surface (AFM)

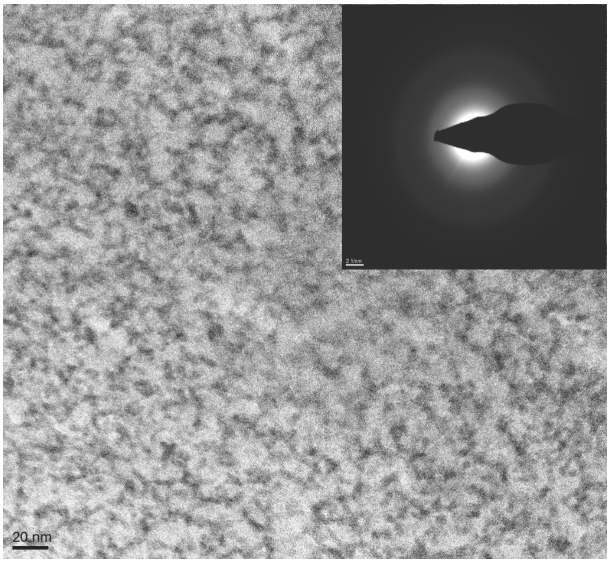

Fig. 3. Structure of the DLC layer with corresponding SAED pattern

It was found by examining thin lamellas from the cross section of CrAlSiN layer produced by PVD technique that the layer features a compact structure with high homogeneity and a grain size is less than 10 nm. It can be concluded already based on TEM images in the bright field that the layers have a nanocrystalline structure. Dark areas appearing on the light field image are crystallites that are oriented close to the axis of bands relative to an electron beam (Fig. 4). Observations in the dark field and the diffraction images made for increasingly smaller areas confirm a nanocrystalline structure of the examined nitride layers.

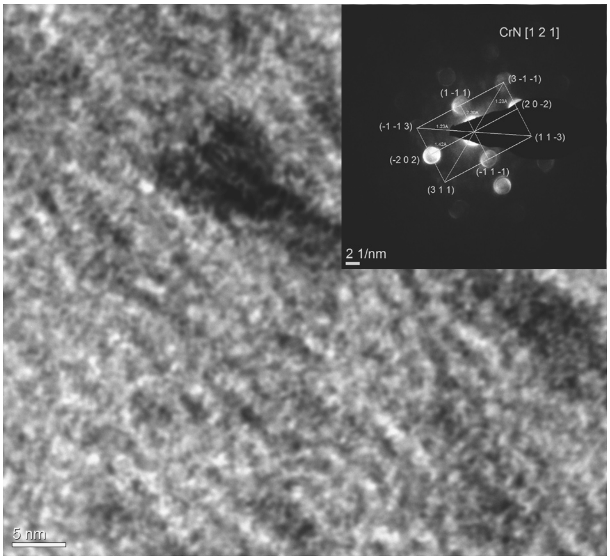

Fig. 4. Structure of the CrAlSiN layer with corresponding microdiffraction

In addition, small crystalline CrN (CrAlSiN) grains sized several nanometres deposited in an amorphous Si_3N_4 matrix were observed in the tests of the CrAlSiN nitride later structure by means of high-resolution transmission electron microscopy, which may signify a layer's nanocomposite structure (Fig. 5).

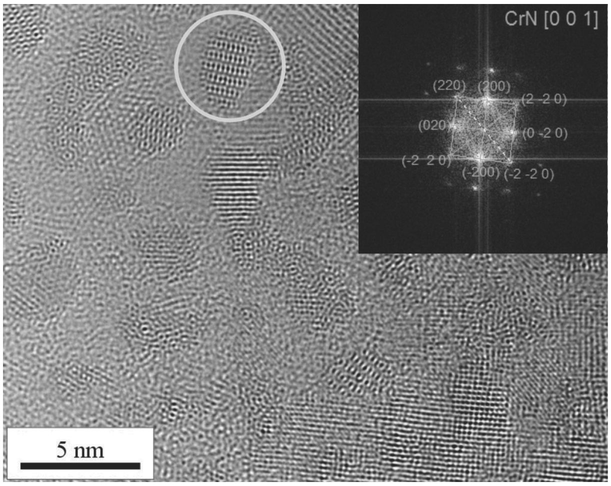

Fig. 5. High-resolution (HRTEM) image of the CrAlSiN layer as well as indexed Fourier transform of the marked area

Moreover, to fully identify the structure of a DLC layer produced with the PACVD method, tests were carried out using a Raman spectrometer (Fig. 6). Raman spectroscopy is a very useful method in diagnosing different carbon phases and also allows to determine 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}).

A Raman spectrum obtained is presented as a sum of two Gauss curves occurring for the Raman offset value of approx. 1359 cm^{-1} (D band), characteristic for sp^3-type bonds, i.e. for diamond and 1581 cm^{-1} (G band) corresponding to sp^2-type bonds, i.e. graphite. The visible 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 quotient of intensity of reflexes corresponding to the phases of diamond and graphite was $I_D/I_G = 1.1$.

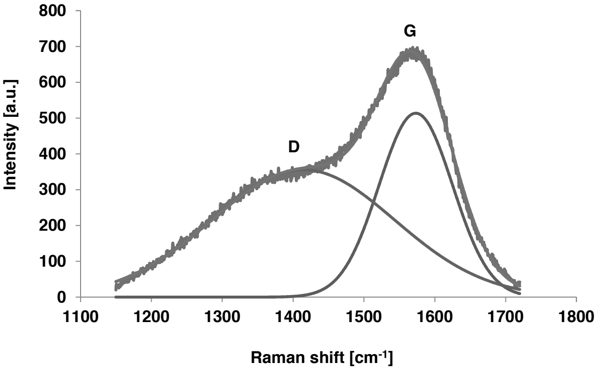

Fig. 6. Raman spectrum of low-friction DLC coating formed with PACVD method

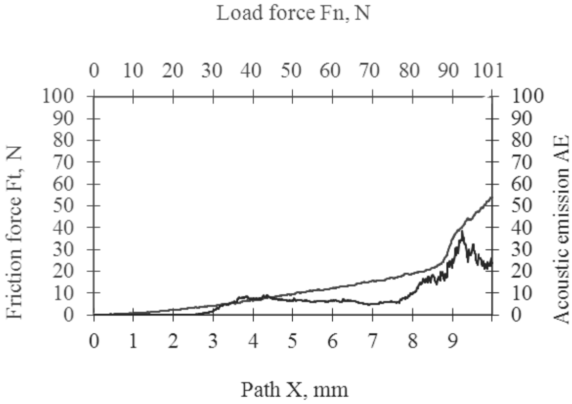

Fig. 7. Diagram of dependence between acoustic emission (AE) and friction force Ft and load for CrAlSiN+DLC coatings

Coating adhesion of the substrate material is one of the crucial concepts concerning the deposition of hard ceramic material onto tools. The critical load L_{C1} and L_{C2} values were determined with a scratch test with a growing load allowing to determine the values of the force causing coating damages. The load at which the first coating damages occur is termed in the literature as the first critical load L_{C1}. This damage is represented by a first weak acoustic emission signal (Fig. 7). A value of the first critical load is related to cohesion damages connected with the chipping of a material inside the coating, without exposing (uncovering) the substrate material, though (Fig. 8a). The second critical load L_{C2} is characterised by the total destruction of a coating. This damage is considered to be a bending point of a rising friction force curve on the chart. This point corresponds to the first contact of a diamond indenter on the substrate when extensive coating chipping takes place (Fig. 8b). Acoustic emission and friction force patterns have their curve disturbed behind this point. The values of the critical load L_{C1} and L_{C2} of investigation coating account for, respectively, 36 and 76 N.

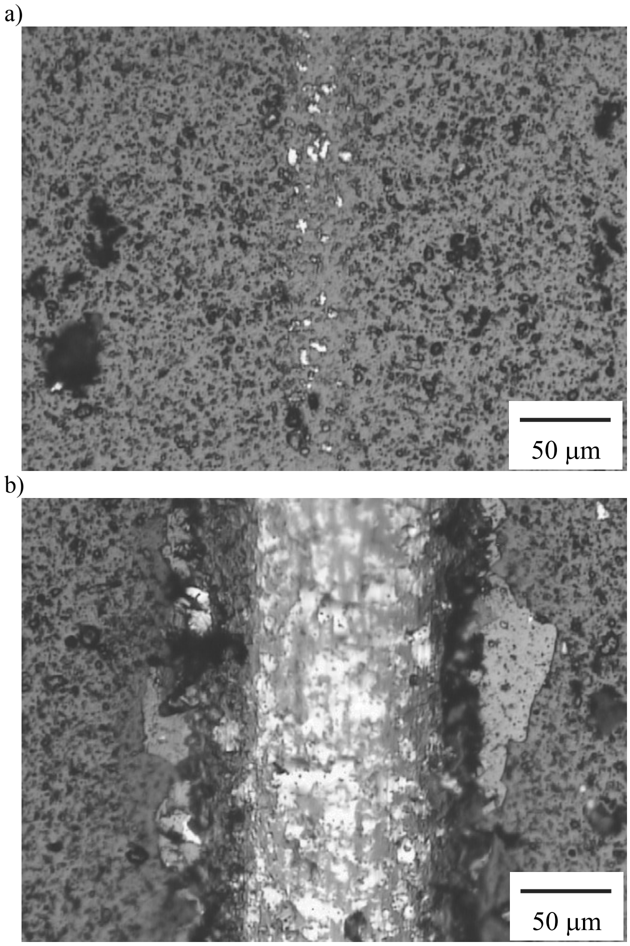

Fig. 8. Scratch mark of CrAlSiN+DLC coating surface with diamond indenter in the scratch test method with critical load of: a) L_{C1}, b) L_{C2}

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. Figure 9 illustrates the diagram 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 23°C for a wear track of 1000 m. The friction curve has a characteristic, with the initial transient state with an unstabilised curve, during which a friction coefficient decreases as the wear track increases until the set state is reached, which usually takes place after approx. 100-200 m. The registered friction coefficient for the examined combinations stabilises within 0.03-0.05 in the conditions of dry technical friction, after the a running-in period.

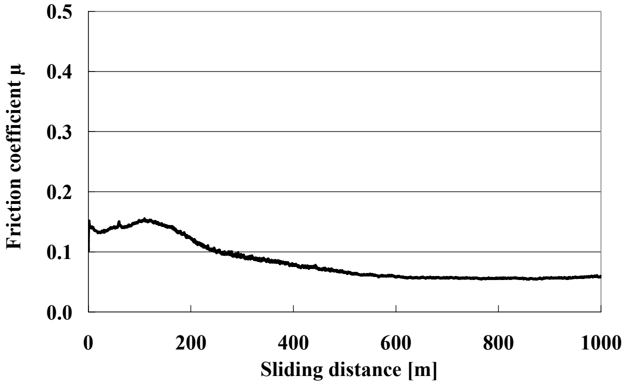

Fig. 9. Dependence of friction coefficient on sliding distance during the wear test for CrAlSiN+DLC coating

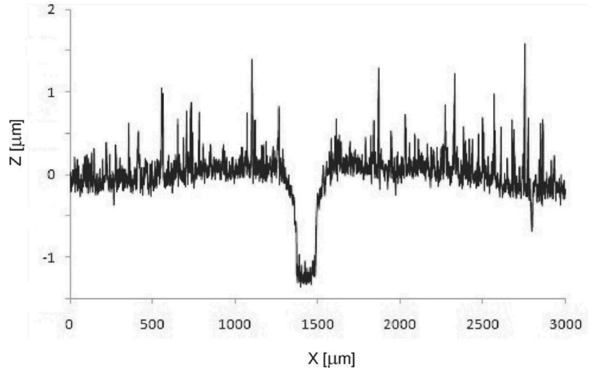

Fig. 10. Wear pattern profile after the wear test of CrAlSiN+DLC coating

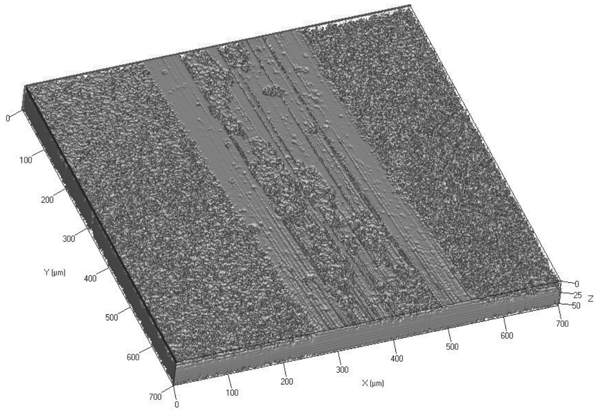

Fig. 11. Three-dimensional surface topography of worn CrAlSiN+DLC coating, confocal microscopy

The coating was not worn through entirely in any of the cases as the maximum depths of wear are smaller than its thickness (Fig. 10). The visible build-ups on the wear surfaces of the tested specimen (Fig. 11) may influence deviations in the friction coefficient on the charts recorded during wear tests.

4. Summary

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

- tests using the transmission electron microscopy confirmed an amorphous character of a low-friction DLC layer,
- with regard to the layers formed with the PVD technique, the size and shape of grains was determined based on the structure obtained using the dark field technique and based on electron diffractions obtained signifying a nanocrystalline structure of the analysed layer and a grain size between 5 to 10 nm,
- the CrAlSiN+DLC coating shows a good adhesion to the substrate; this may be evidenced by the high values of the critical load L_{C2} of the coatings analysed,
- under the technically dry friction conditions, the friction coefficient for the investigated coating is within the range 0.03-0.05.

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