Characterization and Properties of Diamond-Like Carbon Coatings

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Abstract. The paper presents the results of the research on the tribological properties of the DLC coating. The coating was applied using plasma-assisted chemical vapour deposition (PACVD). The obtained coating was determined to be a DLC coating using a Raman spectroscope. Friction tests were performed using a tribometer working in a ball-disc friction configuration at various loads applied. For the tests, a disc with a DLC coating was used as a sample, and a ball made of 100Cr6 steel was used as a counter-sample. The friction tests were carried out in the conditions of technically dry friction. Examination of the coating was done using a scanning microscope. Analysis of the geometric structure of the sample before and after the friction test was performed using a confocal microscope with an interferometric mode. The obtained test results indicated that the properties of DLC coatings are influenced by the deposition process conditions: the argon and methane flow ratio. Whereas the deposition time influences the tribological properties.

Introduction

DLC coatings have aroused great scientific and industrial interest since the beginning of the 70s due to their very good mechanical, physical [1], tribological and anti-corrosion properties [2]. The coatings have a very smooth surface [3–5], high hardness [1,3–6], low friction coefficient, high wear resistance [1,3,4,7,8], good thermal conductivity, high transparency [1,5], good chemical inertness [1,4–6] and biocompatibility [1,4,7,9]. In addition, the coatings can be applied for protective purposes, e.g. to protect other surfaces against corrosion [10,11].

Thanks to all these properties, DLC coatings have been widely used in the production of magnetic disks [5], cutting tools [3,5], mechanical parts, biomedical and optics devices etc. [5].

The DLC coating consists of hybridised bonds of sp1 type (acetylene-like), sp2 type (graphite) and sp3 type (diamond) [1,5,12]. The content of sp2 and sp3 bonds affects the optical, electrical and mechanical properties of the coating [1,5]. It is believed that sp2 and sp3 bonds also have an influence on some biomedical properties [1]. The relatively high content of sp3 hybridisation guarantees very good mechanical properties: Young's modulus of about 300 GPa, hardness above 17 GPa and the friction coefficient lower than 0.05. The physical and mechanical properties of the resulting (modified) surface depend on the type of substrate, method of deposition, layer thickness, applied precursors, etc. [4].

Currently, various methods of DLC coating deposition are used. Essentially, the methods can be divided into two groups: chemical vapour deposition (CVD) and physical vapour deposition (PVD) [3].

Raman spectroscopy is used to examine DLC coating. This method is widely used due to its comparability and non-destructive testing process [5].

When analysing DLC coatings using Raman spectroscopy, a characteristic band is visible in the area of 1000-1700 cm^{-1}, which is band D and band G. The sp2 carbon atoms are centred in around 1355 cm^{-1} to 1550 cm^{-1} 1. The G band is called the graphite band and the D band is the "disorder" band from which useful information can be derived about DLC coating binding characterised by hardness and chemical composition. Raman spectra are used to determine sp2 bonds and the sp2/sp3 bonds ratio [6].

Ižák et al. [6], during their research, applied DLC coatings using the physical vapour deposition method with a pulsed arc system at various flow rates Ar and/or N2, various numbers of pulses and polarization voltage. The resulting coatings were tested with Raman spectroscopy. Changes in the number of pulses and the number of carbon atoms on the samples deposited in the vacuum chamber reflect the thickness and morphology of the DLC layers.

The paper describes a carbon coating tested with a Raman spectrometer to check if DLC was formed. Additionally, selected tribological properties of the deposited layer were examined.

Material and Method

The coating was deposited using the physical vapour deposition method (PVD) and plasma-assisted chemical vapour deposition method (PACVD). A Nanomaster NPE-4000 device was used for this purpose.

The sample was initially cleaned and then put into the chamber of the NPE-4000 device. A vacuum of approx. $3.5 \cdot 10^{-5}$ Torr was generated for this test. Then the sample was cleaned in a vacuum using argon. The cleaning procedure was continued for 15 minutes. Chromium interlayer was deposited between the substrate and the DLC coating, to ensure adhesion of the coating to the substrate. The chromium deposition process took 30 minutes. The chromium interlayer was applied using the PVD method. A chrome target was used for the chromium application. DLC coating was applied using the PACVD method with the parameters given in Table 1.

Tabele 1. The coating application parameters

Cleaning				Interlayer				Coating			
Ar	CH_4	time	RF	Ar	CH_4	time	DC	Ar	CH_4	time	RF
30	0	15 min	200 W	30	0	30 min.	200 W	50	10	2 godz.	150 W

The resulting coating was tested to check if the obtained coating is a diamond-like coating. A Raman spectrometer was used for the test.

While using a scanning electron microscope Phenom XL equipped with an EDS microanalyser, the elements contained in the sample used were observed and identified

Tribological tests were conducted on a TRB^3 working in the ball-on-disk pair in a reciprocating motion. The tests were conducted with the parameters summarized below:

- load P = 10 N i 1N,
- sliding speed v = 0.02 m/s,
- number of cycles = 10 000,
- moisture content 24 ± 2%,
- ambient temperature $T_0 = 25 \pm 2$˚C,
- friction combination: steel ball (100Cr6, 6 mm) – discs with DLC coating.
- technically dry friction.

After the tribological tests the linear wear, friction coefficient and wear area were analysed. The wear area were observed using a confocal microscope with Leica DCM8 interferometric mode.

Results and Discussion

The obtained coating was examined using a Raman spectrometer. Figure 1 shows the obtained examination results.

The obtained test results proved that the coating produced is a DLC coating. The spectrum obtained is typical for this kind of coating, namely the G and D bands are in the spectral range of 1200 to 1700 cm^{-1}. This is a characteristic feature of carbon structures containing graphite-like phases.

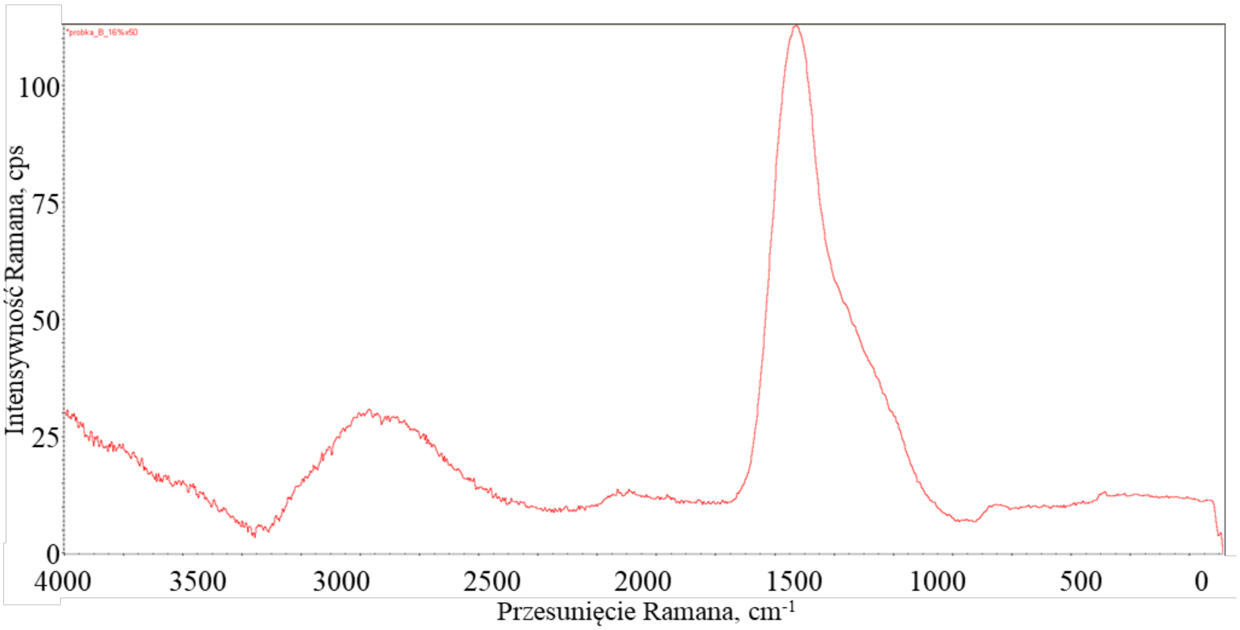
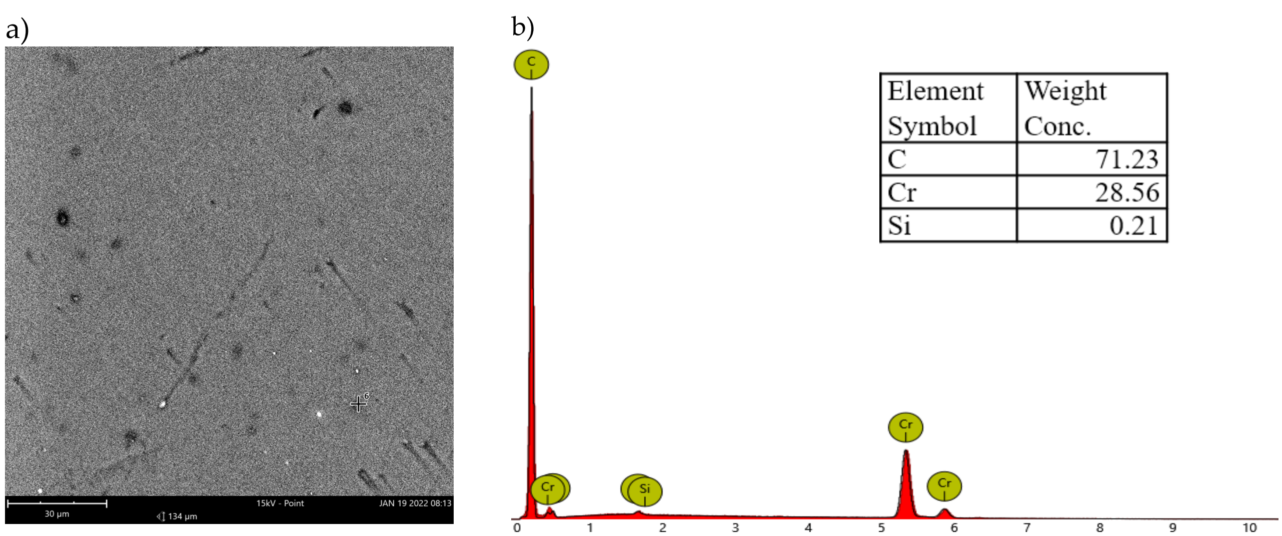


Fig. 1. Raman spectrum for the resulting coating.

Additionally, the deposited layer was examined using a scanning electron microscope equipped with an EDS analyser to check its chemical composition (Fig. 2).



Element Symbol	Weight Conc.
C	71.23
Cr	28.56
Si	0.21

***Fig. 2.** SEM: a) view of the coating and b) the X-ray spectrum together with the chemical composition in the micro-area.*

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The resulting coating is a DLC coating as a high carbon content was identified. Chromium was also observed as it was deposited in the interlayer. The coating obtained was as intended. Figure 3 shows isometric images and primary profiles of the disc before friction tests.

When analysing the maximum wear depth and areas of the discs, it was observed that the abrasion marks found on the disc with the a-C:H coating after technically dry friction were larger for the load of 10 N than for the load of 1 N. The maximum depth was more than half as large, and the worn area was 3.5 times larger. The abrasion mark on the disk was also wider for the higher load case.

Figure 4 shows isometric images and primary profiles of the discs after tribological tests.

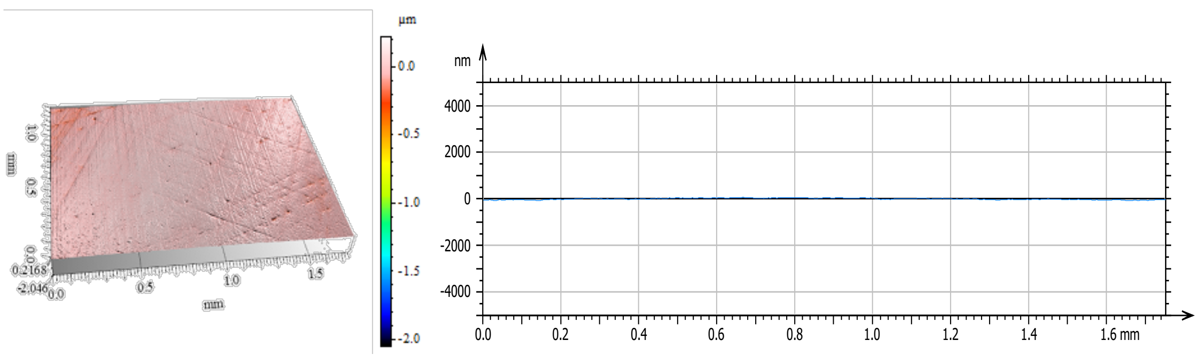
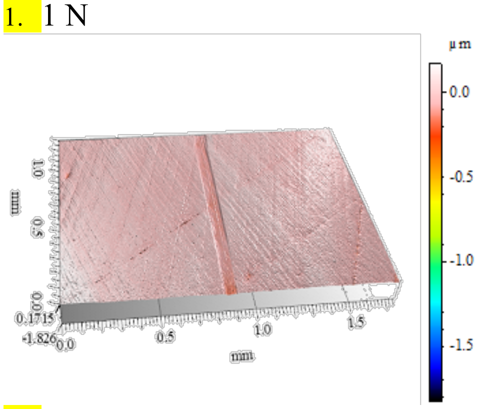
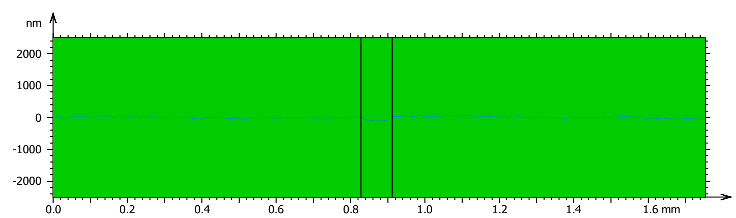


Fig. 3. *Surface textures before the tribological tests: isometric views and primary profiles the a-C:H coating.*

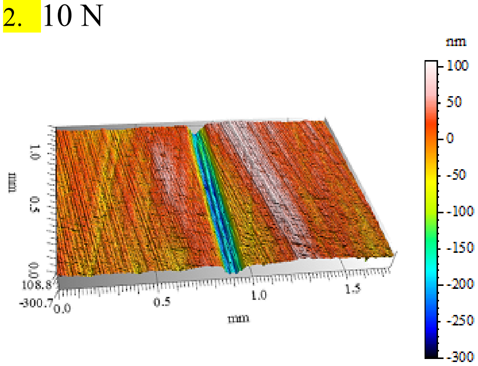
1. 1 N

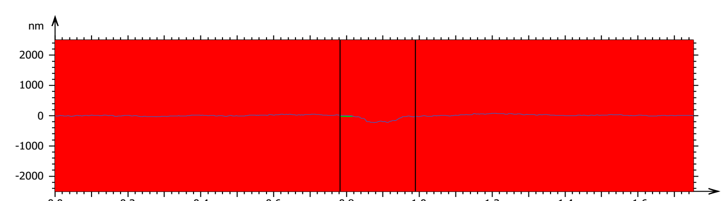




Max. depth	115.4 nm
Wear scar area	6 712 013.0 nm^2

2. 10 N





Max. depth	238.5 nm
Wear scar area	23 629 975.0 nm^2

Fig. 4. *Isometric views and primary profiles of the discs and balls after the tribological tests.*

Table 2. *Surface texture parameters for the disc with coating DLC and before and after the tribological tests.*

Surface texture parameters	Before test	Past test	
		1 N	**10 N**
Sa [nm]	12.38	32.07	30.44
Sq [nm]	15.39	38.77	37.48
Sp [nm]	46.05	109.1	114.7
Sv [nm]	53.18	115.4	121.5
Sz [nm]	99.22	224.5	236.1
Ssk [-]	-0.30	0.65	0.39
Sku [-]	2.83	2.54	2.70

Table 2 presents the roughness of the discs before and after the tribological tests. When comparing the obtained parameters of the geometric structure of the disc surface, lower values of Sp, Sv, Sz, and Sku were found after technically dry friction for the lower load case (1 N). The value of the Sku parameter in all tested cases of the discs was close to 3, which is close to normal distribution. The distribution of unevenness on the measured surfaces was even [13]. Figure 5 shows results after the tribological tests.

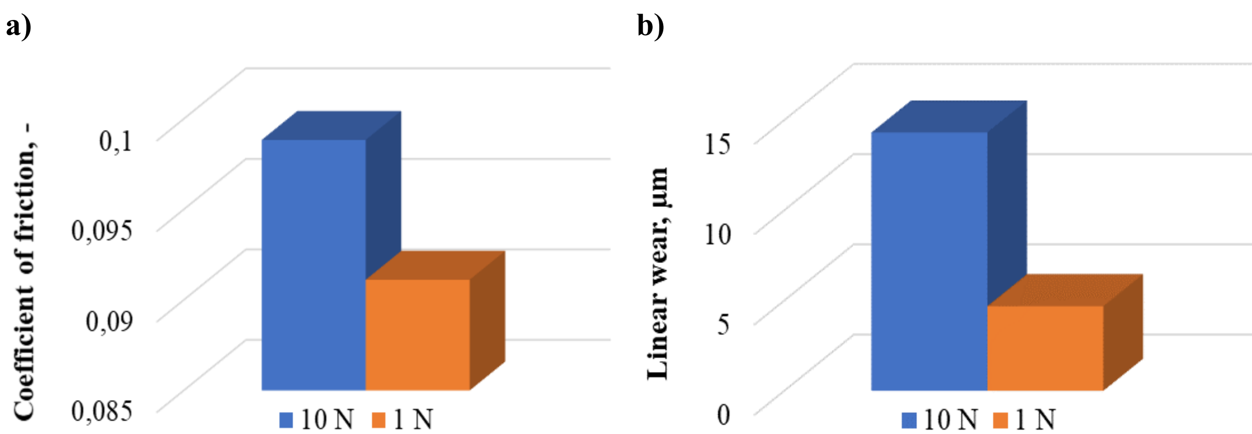


Fig. 5. *a) Coefficient of friction and b) linear wear.*

The wear process causes degradation of the material's strength properties. It occurs due to the interaction of load, such as pressure, thermal and chemical processes [14].

When analysing the results of tribological tests, it was found that lower values of the friction coefficient and linear wear were obtained during the test with a load of 1 N than the test with a load of 10 N. The values were lower by approx. 8% and 67%, respectively.

Summary

To sum up, the following conclusions were drawn from the research results obtained:

1. The tribological properties of the resulting coatings are influenced by the deposition conditions, such as the time and the substrate on which the coatings are deposited.
2. Raman spectroscopy is necessary to determine the type of coating formed. The results of these tests confirmed that diamond-like coatings were produced. A typical spectrum for DLC coatings was obtained. Bands G and D in the spectral range of 1200 to 1700 cm^{-1} were observed.

3. Based on the analysis of the chemical composition performed with a scanning electron microscope equipped with EDS, it was determined that the coating consisted of carbon and chromium. Carbon came from the coating and chromium from the interlayer.
4. When analysing the results of tribological tests, it was found that higher loads translate into a higher friction coefficient and greater linear wear.

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