INFLUENCE OF SUBSTRATE POLARISATION IN THE MAGNETRON SPUTTERING PROCESS (HIPIMS) ON SP^3 BONDS CONTENT IN DEPOSITED DLC COATINGS

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Abstract

DLC (Diamond-Like Carbon) coatings have found applications in various industries due to their unique mechanical properties and wear resistance, which are closely related to their structure. These coatings exhibit a high ratio of sp^3 to sp^2 bonds among carbon atoms. In the present work, DLC coatings were deposited by High Power Impulse Magnetron Sputtering method using several different substrate polarisation values with different Ubias in the range: - 25 V, - 50 V, - 75 V, - 100 V, - 125 V. As the substrates 316L steel with a Cr-CrN coating, aimed at enhancing both the adhesion of the DLC coating and its mechanical properties, was used. In order to analyse the phase composition of DLC coatings, the Raman spectroscopy method was used. Mechanical properties were investigated by the nanoindentation method by using nanohardness tester from Anton Paar with Berkovich diamond indenter. The results of tests showed that DLC coating deposited with substrate polarisation - 50 V had the biggest content of sp^3 bonds and the best mechanical properties.

Keywords: DLC, magnetron sputtering, hybridisation, sp^3

1. INTRODUCTION

The expectation of the industry regarding new types of coatings required the development of not only new material solutions but also new technological solutions. Coatings diamond-like carbon turned out to be one of the most innovative and at the same time very effective application directions of development in the area of surface engineering. DLC (diamond-like carbon) coating is a metastable form of amorphous carbon containing a significant content of sp^3 bonds [1]. Coatings of this type are characterised by properties such as high hardness, modulus of elasticity, chemical resistance and friction-wear resistance, making them widely used in many fields such as medicine, aerospace, cutting tools [2-4]. The dynamic development in the area of innovative carbon-based coatings has contributed to the development of methods for their creation. The High Impulse Power Magnetron Sputtering (HIPIMS) method stands out among the many methods of producing carbon coatings [5]. This method uses a pulsed current-voltage power supply, protecting the source material from overheating and ensuring process stability [6]. The very high power during each pulse effectively protects the target from poisoning, making the coating deposition process stable and fast [7]. This work is focused on the influence of different substrate polarisation (U_{bias}) values during the depositon process on the properties of coatings. The Raman spectroscopy method was used for analysing the phase composition (content of sp^3 bonds) of the obtained coatings. Naoindentation was used to confirm the correlation between phase composition and mechanical properties of DLC coatings.

2. MATERIALS AND METHODS

2.1. Samples preparation

It was necessary to select the substrate U_{bias} voltage value, in order to produce multilayer Cr-CrN-DLC coatings with the highest sp^3 phase content in the DLC layer, which would guarantee the best mechanical properties. The process parameters of the Cr-CrN-DLC multilayer coatings prepared to evaluate the sp^3 phase content in the DLC component layer as a function of substrate Ubias voltage changes are shown in **Table 1**.

Table 1 Process parameters for deposition of multilayer Cr-CrN-DLC coatings

Atmosphere composition	Pressure p [mbar]	Power P [W]	Substrate polarisation voltage U_{bias} [V]	Temperature T [°C]	Pulse frequency f [Hz]	Pulse duration τ [µs]
Cr layer						
100% Ar	0.005	525	- 50	200	1000	60
CrN layer						
85% Ar 15% N_2	0.008	480	- 150	200	1000	50
DLC layer						
100% Ar	0.008	460	- 25	200	1000	50
			- 50			
			- 75			
			- 100			
			- 150			

The technological processes were carried out at the Surface Engineering Centere located at Łukasiewicz-Institute for Sustainable Technologies. The technological device was equipped with two TORUS 4“ magnetrons from K.J.Lesker appointed with targets (graphite target – 99,99% purity, chrome target – 99,99% purity). **Figure 1** shows the chamber during the deposition process of the coatings.

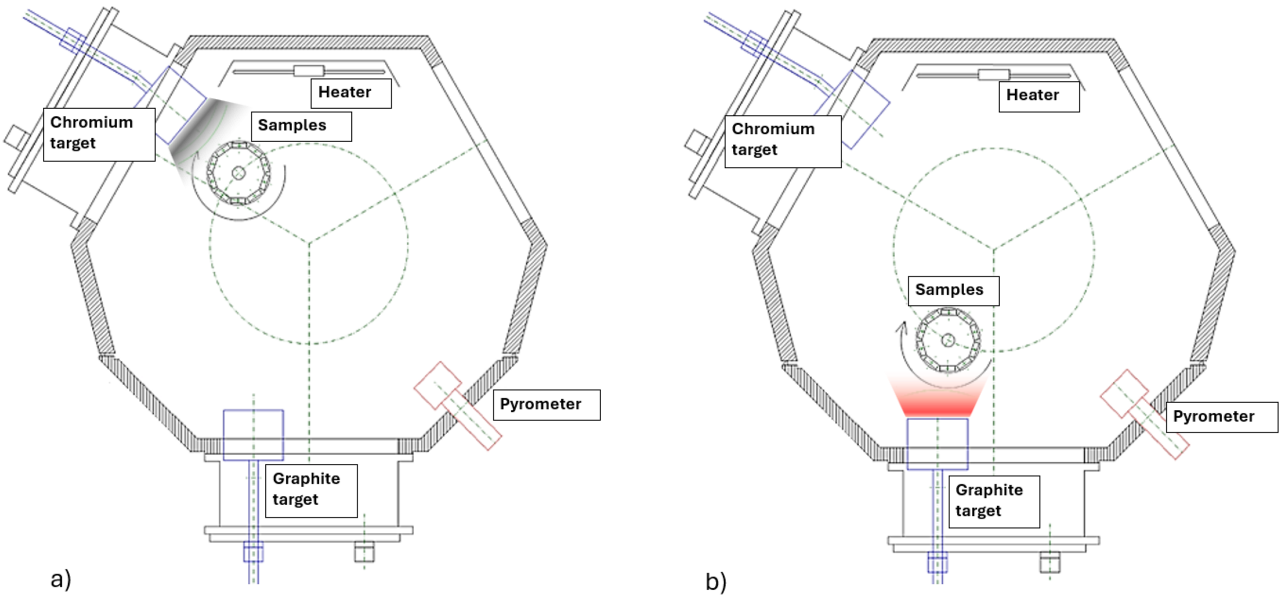

Figure 1 The scheme of vacuum chamber with graphite and chromium targets installed on the wall

Figure 2 shows the model of the deposited coating. According to the assumed scheme, the Cr-CrN-DLC multilayer coating consists of 3 component layers: a diamond-like carbon layer, a chromium nitride - CrN layer and a metallic chromium - Cr layer. The DLC outer layer is responsible for granting anti-wear properties to the coated material. In turn, the function of the CrN and Cr component layers is to ensure proper adhesion of the DLC coating to the steel substrate, as well as sufficient resistance of the entire multilayer coating to external mechanical loads. Austenitic steel 316L was chosen as the substrate.

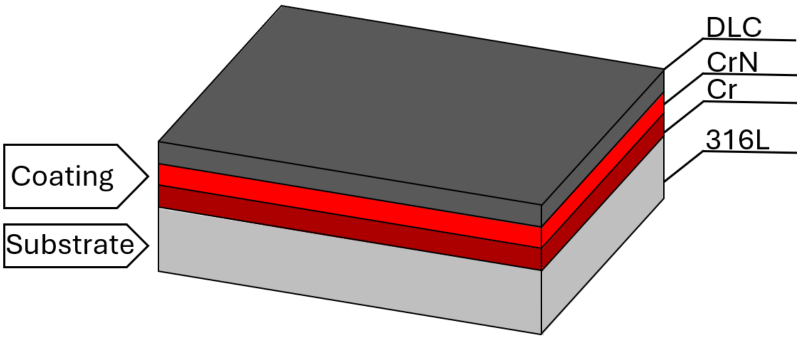

Figure 2 The diagram of the DLC coating consists of Cr, CrN and DLC on the top

2.2. Phase composition analysis

Phase composition was examined with using Raman spectrometer (JASCO NRS – 5100). The device was operating in backscattering geometry and an Ar^+ VIS 2.33 eV (532 nm) light source was used as the radiation source was. In order to balance the intensity levels on both sides of the presented spectrum the vibration spectra were interpolated and their background was removed. The position, intensity and FWHM (full width at half maximum) of the G peaks, which are specific for carbon layers, were compared for all created coatings. To determine sp^3/sp^2 ratio the curve-fitting procedure was used.

2.3. Mechanical properties examination

The nanoindentation method was used for the hardness and Young’s modulus measurements. All prepared samples were examined using NANO-HARDNESS TESTER CSM, equipped with a 65º pyramid-shaped Berkovich indenter. To avoid the influence of the substrate on the results obtained, hardness and Young's modulus measurements were carried out in limited indentation mode, not exceeding 10% of the total coating thickness. For each of the tested samples were performed 20 measurements of hardness and Young’s modulus. Then, 10 mean values were determined from among 10 representative measurements.

3. RESULTS

3.1. Phase composition

In order to create DLC coatings with the best mechanical properties, it was necessary to optimise the process parameter of substrate polarisation. For this purpose, DLC coatings were produced using the following substrate polarisations: - 25 V, - 50 V, - 75 V, - 100 V, - 150 V and investigated using Raman spectroscopy. The application of this testing technique allowed us to determine for which value of the optimised parameter the DLC coating with the highest sp^3 fraction would be produced. **Figure 3** shows a summary of the occurrence of characteristic G and D w peaks for amorphous carbon in the Raman spectral range.

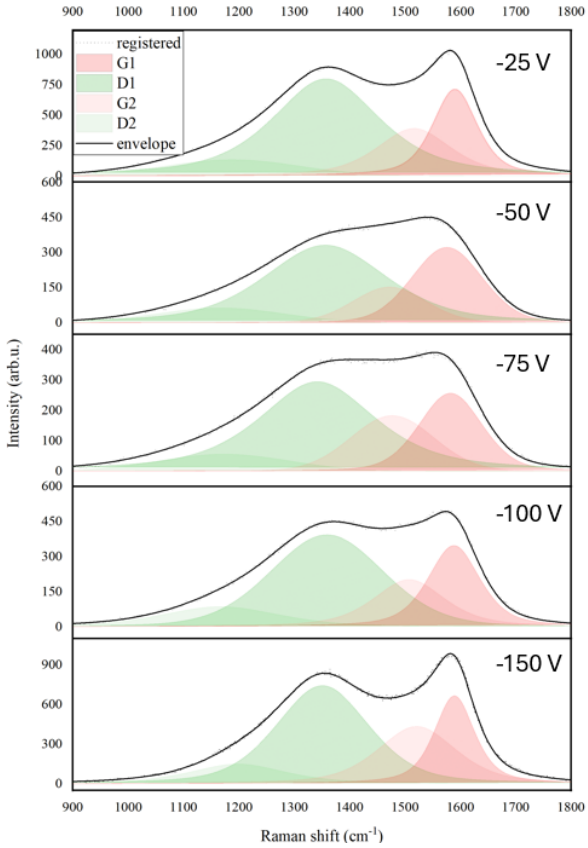

Figure 3 Comparison of Raman spectra of DLC coatings deposited with different values of U_{bias}

Doublets of G and D peaks appear in the Raman spectra. The carbon layers include carbon with a high degree of amorphisation (G1 and D1 peaks) and carbon in the form of carbon nanoclusters with sp^2 hybridisation (G2 and D2 peaks). The elementary components of the Raman spectrum occupy different positions and adopt different half-widths. The position of the G1 peak and the width of the G1 peak are particularly important. These are specific features that indicate amorphisation of the carbon layer. FWHM of G peak is connected with structural disorder, and the G-band position is related to topological disorder [8]. On **Figure 4** the evolution of the G1 peak position and its half-width (FWHM) is shown.

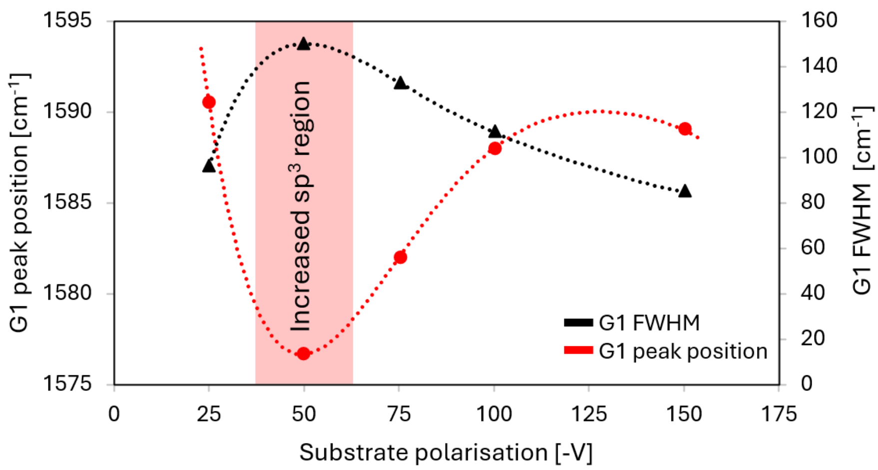

Figure 4 Changes in the position of the G peak and its half-width (FWHM) as a function of substrate polarisation voltage

The dependence of the position of the G peak and its FWHM, on the polarisation, indicates the existence of some extremes for the DLC coating deposited at a substrate polarisation of - 50 V. It can be judged from this that this coating has an increase in sp^3 bond content. The nature of the Raman spectra indicates the existence of a certain fraction of carbon in it with relatively high amorphisation.

3.2. Mechanical properties

The nanoindentation tests were performed on the DLC coatings produced at the following substrate polarisations: - 25 V, - 50 V, - 75 V, - 100 V, - 150 V and their average values are shown in **Figure 5**.

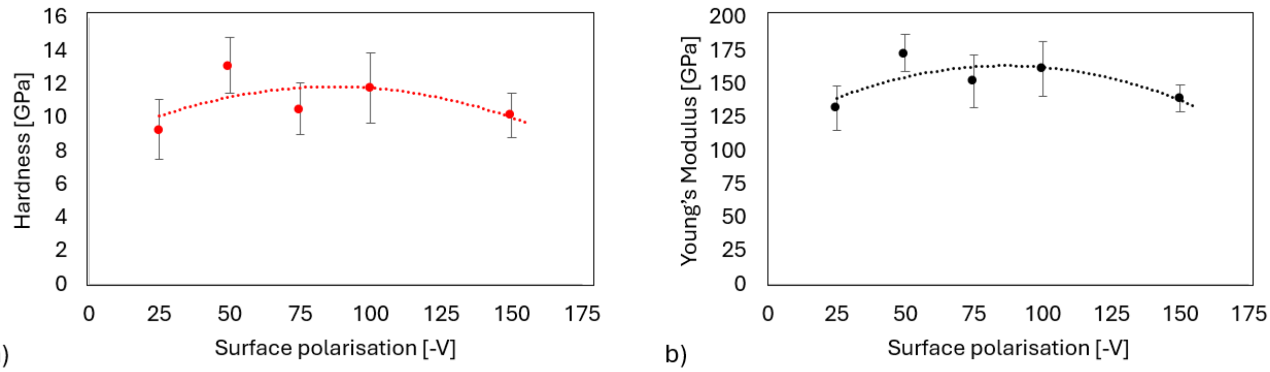

Figure 5 Results of hardness and Young's modulus measurements for a DLC layer produced with different substrate polarisation

The coating created at a substrate polarisation of - 50 V has the highest values of hardness (H = 13 GPa) and Young's modulus (E = 175 GPa). After reach this one maximum values of hardness and Young' s modulus ares stabilizing and then decreased slightly. Based on the analysis of these values and the results of Raman spectroscopy, it should be concluded that the DLC coatings produced at a substrate polarisation of - 50 V contain the most amorphous sp^3 phase and have the best mechanical properties.

4. CONCLUSION

In this study, the impact of U_{bias} values used during deposition process, on structure and properties of deposited DLC coatings was analysed. Tests carried out on Cr-CrN-DLC coatings, with the DLC layer created with using different values of substrate polarisation, made it possible to select the optimum value for this deposition parameter. The results of the phase composition analysis, performed using Raman spectroscopy, showed that the highest proportion of the sp^3 phase in DLC coatings deposited at a substrate polarisation of - 50 V. Hardness and Young's modulus measurements indicate the best mechanical properties of the DLC coating produced for this value of substrate polarisation, confirming the highest content of the amorphous phase.

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