

*Monika Madej  
Dariusz Ozimina  
Krzysztof Kurzydłowski  
Tomasz Płociński  
Piotr Wieciński  
Michał Styp-Rekowski  
Maciej Matuszewski*

ISSN 1333-1124  
eISSN 1849-1391

## **PROPERTIES OF DIAMOND-LIKE CARBON COATINGS DEPOSITED ON CoCrMo ALLOYS**

### **Summary**

This paper presents results of the structure analysis and tribological testing of a-C:H type diamond-like carbon (DLC) coatings produced by the Plasma Assisted Chemical Vapour Deposition (PACVD) technology on CoCrMo specimens. The DLC coating structure was studied by observing the surface topography using a scanning electron microscope (SEM) in the SE and STEM modes and a profilometer. Raman spectroscopy provided information on hybridized covalent bonds. The structural analysis involved observing the cross-sections of the coatings using a scanning electron microscope (SEM) with an energy dispersive spectrometer (EDS) to determine the concentration and distribution of the constituent elements in the coating. Wear resistance was studied by applying a T-17 pin-on-plate tribological system: a polymeric pin made of ultra-high-molecular-weight polyethylene (UHMWPE) and a CoCrMo plate with a DLC coating. The testing was conducted under friction conditions using Ringer's solution as a lubricant. The test results showed that the application of DLC coatings definitely improves the serviceability of a surface.

*Key words:* diamond-like carbon, coating, chemical analysis, wear-resistant

### **1. Introduction**

Changes resulting from osteoarthritis, especially articular cartilage damage, which are now increasing in number, are chronic conditions of the musculoskeletal system. When the cartilage loses its shock-absorbing ability, the resistance to motion at the joint rises [1, 2]. The most effective method of treatment of advanced osteoarthritis changes is hip replacement. A hip implant enables a greater range of mobility and relieves pain. A tribological system replacing the missing biological structure improves its basic mechanical activities but does not meet the requirements of a human joint [3]. The main types of wear occurring in friction systems of hip joint prostheses include: abrasive wear, plastic strain and creep, fatigue wear –

pitting, and degradation of the polymer element [1, 4, 5]. The major factor affecting the process of wear of the prosthesis frictional elements is the type of material mating; of importance are also unit pressure, surface roughness of the elements in contact, kinematics of the friction joint and a patient's mobility [2, 5]. In References [2, 6-8], the authors present results of experiments concerning the causes of wear of elements made of UHMWPE mated with CoCrMo and CoCrMo coated with DLC. Because of large differences in the process parameters and conditions described in the literature on this topic, the studies give a scatter in results. It should also be noted that the phenomena observed during model tests are very different from those occurring in a human organism. Knowing the important role of lubricants, many researchers include information on the solutions used.

The alloys of the CoCrMo group are now being extensively investigated for wear resistance in a system with ultra-high-molecular-weight polyethylene (UHMWPE). The results obtained by different researchers frequently vary because of different research methods, different process parameters and different lubricants applied [9].

Most investigations on the subject have aimed at improving the hip joint prosthesis design; they have generally not taken account of wear processes. Today, much attention is being paid to the application of new materials to friction systems. An example of such a material is diamond-like carbon. The term diamond-like carbon was coined in 1971 by Aisenberg and Chabot, who produced hydrogen-free amorphous carbon films by cooling them in argon with a low-energy beam of carbon ions [10]. That breakthrough invention initiated extensive studies into carbon films ranging from soft to very hard, with the latter having a resistivity of the order of  $10^{12}$   $\Omega\text{cm}$ . Today's diamond-like carbon coatings cover a great number of amorphous, generally hydrogenated, thin-film materials with various properties, depending on the type of method used and the conditions of the production process. As there are many systems and methods employed to produce such coatings, the materials may have different names: DLC, a-DLC, a-C, a-C:H, ta-C, a-D, i-C, hard carbon, etc. Thus, the same name may be used for different materials, or similar materials may be denoted differently. Amorphous carbon can be a mixture of atoms with  $sp^3$ ,  $sp^2$  and even  $sp^1$  bonds with possible presence of hydrogen. Amorphous carbon materials may differ considerably in structure, and their properties depend on the method of production and process parameters [11, 12]. An equally vital factor that affects their properties is the ratio of the  $sp^2$  bonds present in graphite to the  $sp^3$  bonds in the diamond structure. Amorphous carbon with a high content of diamond  $sp^3$  bonds is known as DLC. When a-C diamond-like carbon coatings are modified with metals, they are denoted as a-C:Me. An a-C:H coating modified with a metal is marked as a-C:H:Me (W, Ti, Nb, Cr, Co, Mo); however, when modified with a non-metal, it is denoted as a-C:H:X (H, Si, F, N, P, B).

Coatings with hydrogenated amorphous carbon (a-C:H) are the ones that have been most investigated so far with respect to biocompatibility (for example, see the studies by Thomson [4], Butter [7], and Allen [6]). Many studies have also focused on a comparative analysis of the effect of doping of DLC coatings with such elements as: Ti, Al, Zr, and N. Adhesion of the DLC coating to the substrate, e.g. an implant, has been of particular significance. It has been found that the substrate adhesion can be enhanced by using a silicon interlayer because of strong Si-C bonds occurring at the interface.

## 2. Materials and methods

### 2.1 Materials

In this study, tests were conducted on the CoCrMo alloy, commercially known as Biodur CCM PLUS, which is characterized by high mechanical strength, corrosion resistance and wear resistance. The alloy was produced by Carpenter's Micro-Melt® powder metallurgy process using the Vacuum Induction Melting (VIM) method. The chemical composition of the alloy – Biodur CCM PLUS – is shown in Table 1, and the most important mechanical parameters are presented in Table 2, from the Carpenter declaration.

**Table 1** Chemical composition of the Biodur CCM PLUS alloy

Chemical element	Co	Cr	Mo	N	C	Ni	Mn	Fe	Si
Content, wt. %	base	26÷30	5÷7	0.15÷0.2	0.2÷0.3	0.3	0.5	0.3	0.6

**Table 2** Mechanical properties of the Biodur CCM Plus alloy

State	Yield strength /MPa	Tensile strength /MPa	Elongation /%	Hardness /HRC	Young's modulus /MPa	Poisson's ratio
Annealed	585	1035	25	30	240	0.3
Warm worked	930	1310	26	40		
Hot worked	760	1100	25	33		

Another material tested was ultra-high-molecular-weight polyethylene (UHMWPE). Its molecular weight measured using a viscosimetric method ranges from 2 to 10 mln. g/mol. Ultra high molecular weight contributes to the development of optimal properties [9, 13]. Table 3 shows the physical properties of the tested UHMWPE specimens, with a commercial name Chirulen.

**Table 3** Physical properties of ultra-high-molecular-weight polyethylene

Property		Value	Standard
Density /kg/m <sup>3</sup>		930-944	ISO 5834
Ash content /ppm		<150	
Compressive strength /MPa	23°C	≥ 21	
	120°C	≥ 3	
Tensile strength /MPa	23°C	≥ 21	
	120°C	≥ 18	
Elongation /%	23°C	≥ 350	
	120°C	≥ 600	
Impact resistance /MJ/mm <sup>2</sup>		≥ 140	DIN 58836
Hardness /Shore D		68	
Abrasive wear /%		≤ 1	

## 2.2 Raman spectroscopy

Measurements were performed using a dispersive microRaman spectrometer (Nicolet Almega XR) with a 532nm (Nd:YAG) 2.5mW laser line. Spectra were registered in a range of 100-4000  $\text{cm}^{-1}$  with a real resolution of approx. 6  $\text{cm}^{-1}$ . The beam was focused using an optical microscope (Olympus B51) including x50 lens. The spectra were decomposed with Nicolet Omnic 8 using a Gaussian profile.

## 2.3 Scanning electron microscopy (SEM)

Specimens – CoCrMo alloy and CoCrMo alloy coated with DLC – were observed before and after tribological tests using scanning electron microscopy. The specimens were prepared for the analysis using a focus ion beam (FIB) setup (Hitachi FB2100). The cross-sections were observed by means of a scanning electron microscope (Hitachi SU 70) equipped with a field emission gun of the Schottky type. During the observations, the specimens were inclined at an angle of 40°, which is a maximum angle for specimens of this size. The characteristics of the coatings visible in the images, e.g. thickness, are lower than in reality. The actual dimensions are obtained at an angle of inclination of 90°. When describing the results, real dimensions are used and the degree of inclination of the specimen is included. The TEM observation was performed by means of a high-resolution scanning electron microscope (Hitachi s5500) equipped with a field emission electron gun operating at a maximum accelerating voltage of 30 KeV. The analysis was conducted in the SE mode (which is a standard mode for SEM) and in the STEM mode, using a beam passing through the specimen. The chemical composition was determined using energy dispersive X-ray spectroscopy (EDS).

## 2.4 Surface texture

The research included measurements of the surface texture of the coated elements, which enabled the analysis of the surface character [14]. A Taylor Hobson Talysurf CCI optical profiler was used. Being a non-contact tool, the profiler offers scanning broadband interferometry (coherence correlation interferometry) giving a high 0.1Å vertical resolution, regardless of the magnification level. The measurement results were registered by a CCD camera with a resolution of 1024x1024 pixels. With more than a million points of the surface registered during one measurement, we can generate a 3D image.

The measured area was 0.33 mm x 0.33 mm, and the measurement range in the Z-axis was 2.2 mm. The TalyMap Platinum software enabled the processing and complex analysis of the measurement data.

## 2.5 Tribological tests

A wear test was performed using a pin-on-plate (T-17) device according to the standard listed as Ref. [15]. The coefficient of friction and the wear rate were determined with respect to the number of cycles. The T-17 system is designed to perform a tribological analysis of different pairs of materials with surfaces in sliding contact moving in a reciprocating motion. The two friction systems tested were: a UHMWPE pin and a CoCrMo plate, and a UHMWPE pin and a CoCrMo plate with a DLC coating. The following parameters were used to test these metal-polymer systems:

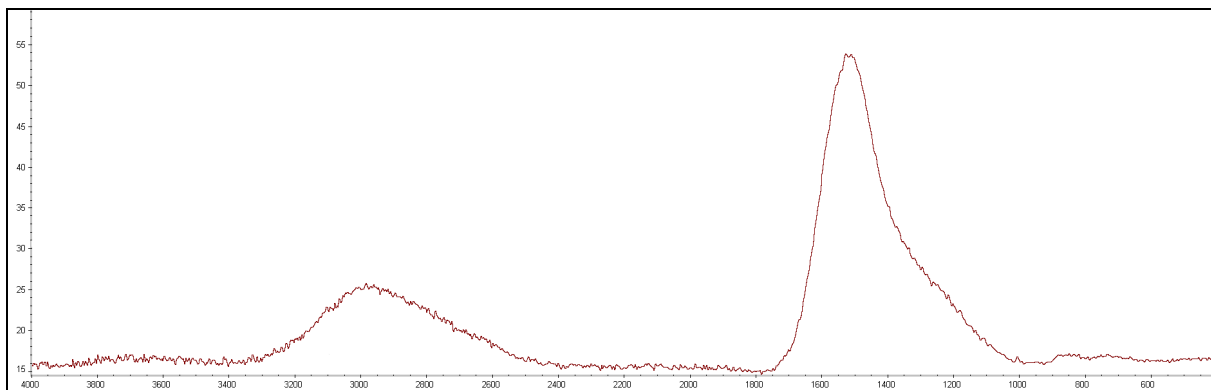
- test duration / number of cycles – 1.000.000 s / 1. 000. 000;
- amplitude – 12.7 mm;
- frequency - 1 Hz;

- average sliding rate - 50 mm/s;
- load - 225 N;
- lubricating fluid – RINGER's solution;
- temperature of the fluid during testing -  $37 \pm 1$  °C.

### 3. Results and discussion

#### 3.1 Raman spectroscopy

In most carbon coatings, the Raman spectrum is dominated mainly by two bands lying around  $1500\text{ cm}^{-1}$ . The spectrum can be decomposed into two lines: one for about  $1580\text{ cm}^{-1}$  (peak G), and the other for about  $1350\text{ cm}^{-1}$  (peak D). Peak G is active in monocrystalline graphite and arises from the chain-like spatial configuration of hybridized carbon  $\text{sp}^2$  bonds. An increase in the irregularity of the graphite structure results in the occurrence of a peak denoted as D. The peak is attributable to the occurrence of the ring spatial configuration of hybridized carbon  $\text{sp}^2$  bonds.  $\text{Sp}^1$  and  $\text{sp}^3$  bonds also form. The correlation between the position and intensity of peaks G and D can be used to determine the physical properties of the coatings. Figure 1 shows the Raman spectrum of the carbon coatings.

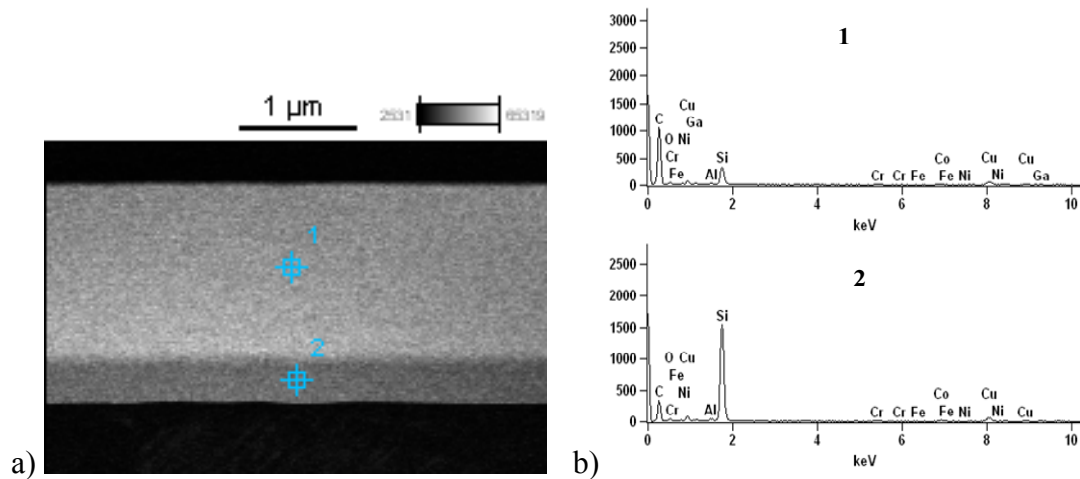


**Fig. 1** Raman spectrum of the diamond-like carbon coating.

The Raman spectrum was decomposed using a Gaussian profile. In this way we obtained information on the position and intensity (I) of the bands. The position of the G band for the a-C:H coating was  $1570\text{ cm}^{-1}$ , whereas that of the D band was  $1364\text{ cm}^{-1}$ . In both cases, the ratio  $I_D/I_G$  was close to 1. Comparing the obtained value with the data presented in Ref. [16], we determined the  $\text{sp}^3$  content in the coatings, which was about 30%. Additionally, the position of the G band was more than  $1550\text{ cm}^{-1}$  for the visible excitation of the Raman spectrum, which also confirms a high content of  $\text{sp}^3$  in the coatings. In the case of the a-C:H coating, the intensity of the Raman spectrum was higher.

#### 3.2 Scanning electron microscopy (SEM)

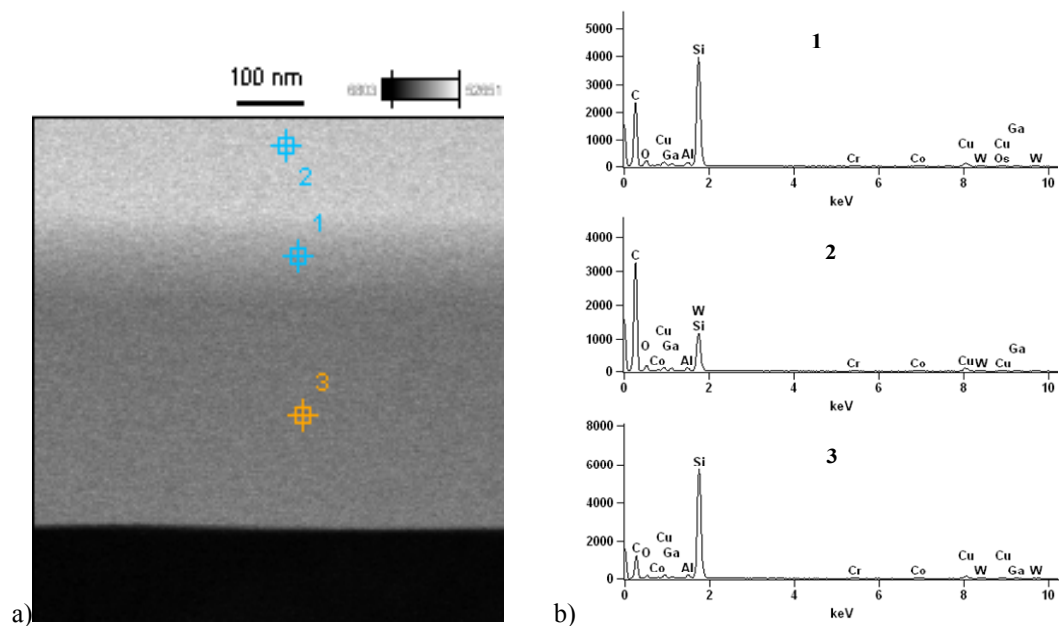
The specimens with deposited DLC coatings were observed by scanning electron microscopy. Results of a quantitative X-Ray microanalysis (EDS) of the subcoatings and the substrate are presented in Figure 2, Figure 3, Table 4 and Table 5.



**Fig. 2** (a) Points of the chemical content analysis of the substrate and the coating;  
(b) characteristic X-ray spectra for the points of the chemical content analysis

**Table 4** Chemical composition (atomic percentage) of the substrate and the coating

	C-K	O-K	Si-K	Cr-K	Co-K	Mo-L
Point 1	99.09	0.00	0.82	0.03	0.06	0.00
Point 2	88.36	5.85	5.59	0.07	0.13	0.00



**Fig. 3** (a) Points of the chemical content analysis of the transitional layer;  
(b) characteristic X-ray spectra for the points of the chemical content analysis.

**Table 5** Chemical composition (atomic percentage) of the transitional layer

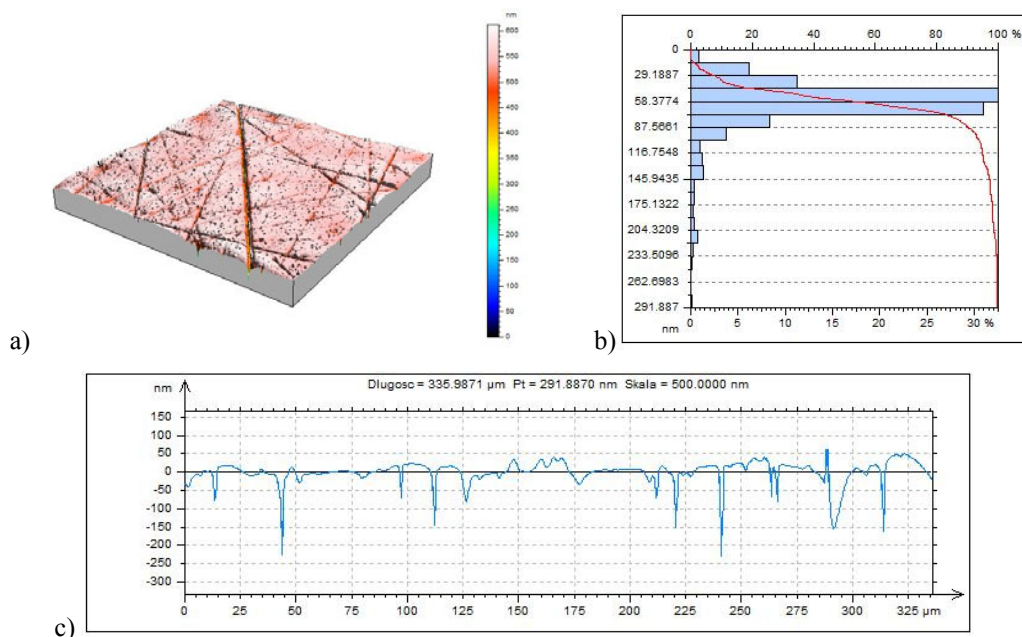
	C-K	O-K	Si-K	Cr-K	Co-K
Point 1	93.53	3.84	2.55	0.03	0.04
Point 2	98.45	0.69	0.80	0.02	0.04
Point 3	89.11	5.19	5.54	0.05	0.11

A quantitative analysis performed with a scanning electron microscope equipped with an energy dispersive spectrometer (EDS) is not suitable for determining the content of carbon. However, it was still possible to draw conclusions about the chemical composition of each subcoating. The outer subcoating is the proper DLC coating containing mainly carbon, while

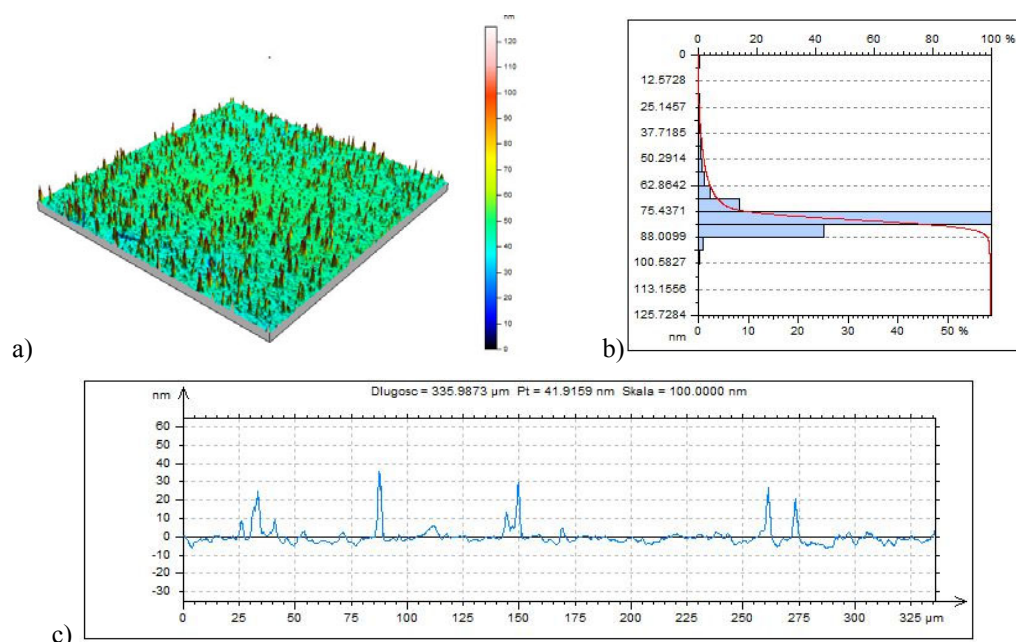
the subcoating lying directly on the substrate is the transitional layer containing mainly silicon, which was partially oxidized. The quantitative analysis of this subcoating, which did not show the content of carbon, indicated the presence of Si (64 % at.) and O<sub>2</sub> (34 % at.) and trace amounts of Cr and Co. The transitional layer contained both carbon and silicon.

### 3.3 Surface texture

The surface texture of the a-C:H type DLC coating was analyzed in detail using 3D images. The surface topography, ordinate distribution with the load curve, and the surface profile of the substrate are shown in Figure 4, while those of the coating materials in Figure 5. Table 6 shows the most important parameters of the surface texture of the specimens.



**Fig. 4** Surface texture of the CoCrMo alloy: a) surface topography, b) ordinate distribution and the load curve, c) surface profile.



**Fig. 5** Surface texture of the a-C:H type DLC coating: a) surface topography, b) ordinate distribution and the load curve, c) surface profile.



**Table 6** Parameters of the surface texture

Surface parameters	CoCrMo alloy	a-C:H coating
$S_a$ /nm	19.8519	4.4890
$S_q$ /nm	34.5613	8.6298
$S_{sk}$	-4.3756	3.6509
$S_{ku}$	35.9247	27.8285
$S_p$ /nm	60.0112	78.2440
$S_v$ /nm	552.8493	125.7284
$S_z$ /nm	612.8605	0.8603

The arithmetic mean of the 3D roughness,  $S_a$ , which is a basic amplitude parameter for the quantitative assessment of the analyzed surface, was higher for the base material – the CoCrMo alloy – than for the a-C:H coating. A similar trend was observed with the root mean square of the 3D roughness,  $S_q$ ,  $S_v$  and  $S_z$ . Other amplitude parameters providing information on the surface texture are skewness,  $S_{sk}$ , and kurtosis  $S_{ku}$ . These parameters are sensitive to the occurrence of local peaks or valleys as well as defects. The parameter  $S_{sk}$  of the CoCrMo alloy had a negative value, which indicated a plateau surface. The high values of  $S_{ku}$ , on the other hand, resulted from the high slenderness of the ordinate distribution curve. The values of these parameters were higher for the DLC coating than for the substrate material. Surface roughness definitely contributed to the tribological properties of the materials.

### 3.4 Tribological tests

The results of tribological testing are presented graphically in Fig. 6. The figure shows the changes in the coefficient of friction  $\mu$  and in the wear rate with respect of the number of cycles. In Fig. 7 we can see the cross-sections of the as-deposited DLC coating and the same coating after tribological tests.

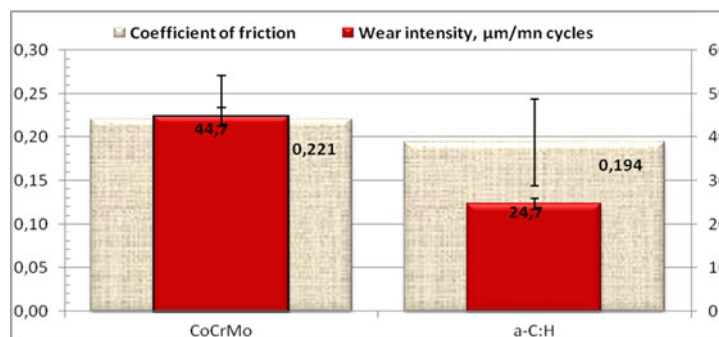


Fig. 6 Coefficient of friction and wear rate vs. the number of cycles for the UHMWPE-CoCrMo and UHMWPE-a-C:H coating systems.

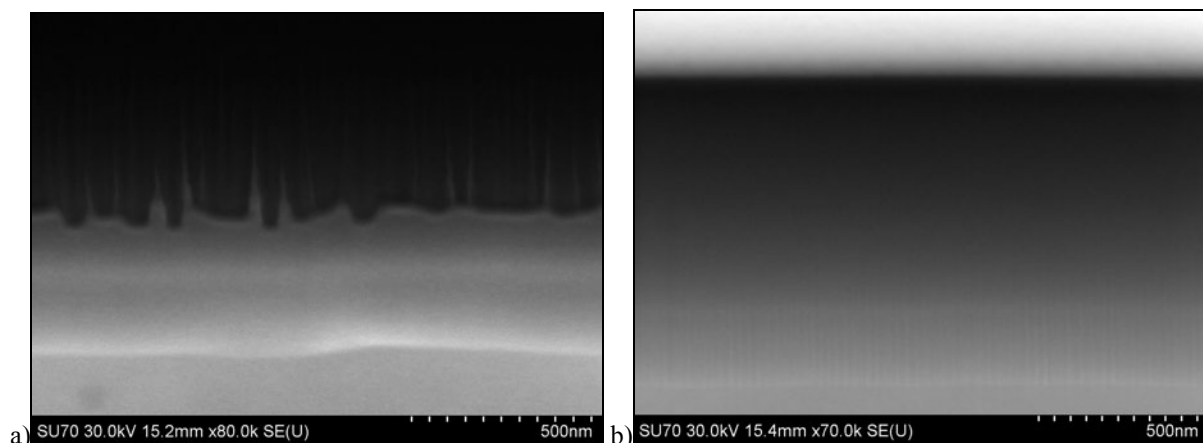


Fig. 7 SEM images of cross-sections of the a-C:H coating a) prior to and b) after tribological tests



The tribological tests revealed that the coefficient of friction and the wear rate were lower for the a-C:H coating than for the substrate material – CoCrMo alloy.

The DLC coating with a total thickness of about 2.10  $\mu\text{m}$  comprised three fundamental areas: a light area, lying directly on the surface, a dark area, being the outer part of the coating, and a transitional area including elongated “needles” extending from the light area (Fig. 7a). The two extreme areas – dark and light – are phases with different chemical compositions (Figs. 2 and 3).

After tribological tests, the total thickness of the coating decreased to 1.51  $\mu\text{m}$  (Fig. 7b). The coating morphology also changed. There was no transitional area between the light and dark phases with needles extending from the light phase. Moreover, the contrast between the light and dark phases was much lower than in the as-deposited coating. The difference suggests that no clear transitional area was observed in that specimen.

#### 4. Conclusions

The most significant findings emerging from this study are as follows.

- The analysis of the properties of the base material – CoCrMo alloy – and the a-C:H type DLC coating obtained by the PACVD method indicates that further research should focus on their application as elements of friction joints, including a hip joint prosthesis.
- The observations of the structure and the analysis of the composition revealed that the structure of the coatings was in compliance with the design specifications. The Raman spectroscopy analysis provided information on the hybridized bonds.
- From the SEM analyses it is clear that the DLC coatings deposited by the PACVD method had a more homogeneous structure.
- The surface texture analysis shows that the a-C:H type coating has better parameters than the base alloy, i.e. CoCrMo.
- The tribological tests showed that the wear resistance of the DLC coating was higher than that of the CoCrMo alloy. The coefficient of friction and the wear rate of the a-C:H coating were considerably lower.

#### REFERENCES

- [1] Shi B., Ajayi B., Fenske G., Erdemir A., Liang H.: Tribological performance of some alternative bearing materials for artificial joints. *Wear*. Vol. 255, 2003. pp. 1015–1021
- [2] Madej M., Ozimina D., Piwoński I., Kisiełowska A.: The properties of diamond-like carbon coatings used for artificial joints. *Kovove Materialy – Metallic Materials*. Vol 4, 2012. pp. 287 - 295
- [3] Lappalainen R., Selenius M., Anttila A., Kontinen Y., Santavirta S.: Reduction of wear in total hip replacement prostheses by amorphous diamond coatings. *Journal of Biomedical Materials Research. Applied Biomaterials*. Vol. 66B, 2003, pp. 410-413.
- [4] Thomson L., Law F., Rushton N., Franks J.: Biocompatibility of Diamond-Like Carbon Coating, *Biomaterials*. Vol. 12, 1991, pp. 37-40.
- [5] Thorwarth G., Falub C., Muller U., Weisse B., Voisard C., Tobler M., Hauert R.: Tribological behavior of DLC-coated articulating joint implants. *Acta Biomaterialia* 6, 2010, p. 2335-2341
- [6] Allen M, Myer B, Rushton N. J. In vitro and in vivo investigations into the biocompatibility of diamond-like carbon (DLC) coatings for orthopedic applications. *Biomedical Materials Research B*. Vol. 58, 2003, pp. 319-328.
- [7] Butter R., Allen M., Chandra L., Lettington A. H., Rushton N.: In vitro studies of DLC coatings with silicon intermediate layer. *Diamond and Related Materials*. Vol. 4, 1995, pp. 857-861.

- [8] González-Mora V., Hoffmann M., Stroosnijder R., Gil F.: Wear tests in a hip joint simulator of different CoCrMo counterfaces on UHMWPE. *Materials Science and Engineering C*. Vol. 29, 2009, pp. 153-158.
- [9] Kurtz S.: *UHMWPE Biomaterials Handbook*. Elsevier 2009.
- [10] Aisenberg S., Chabot R.: Ion-beam deposition of thin films of diamond like carbon. *Journal of Applied Physics*. Vol. 42, 1971, pp. 2953- 2958.
- [11] Ozimina D., Madej, M.: Properties of single and multi-layer DLC coatings. *Tribologia*. Vol. 2, 2010, pp. 119-136.
- [12] Michalczewski R., Piekoszewski W.: Wear and friction of low friction coatings in dry conditions. *Finnish Journal of Tribology*. Vol. 26, 2007, pp. 9–21.
- [13] Liu H., Xie D., Qian L., Deng X., Leng Y., Huang N.: The mechanical properties of the ultrahigh molecular weight polyethylene (UHMWPE) modified by oxygen plasma. *Surface & Coatings Technology*. Vol. 205, 2011, p. 2697.
- [14] Adamczak S. *Measurements of the surface geometry*, Warszawa, WNT 2009.
- [15] ASTM 732-82. Reciprocating pin-on-flat evaluation of friction and wear properties of polymeric materials for use in total joint prostheses.
- [16] Ferrari A, Robertson J. Interpretation of Raman spectra of disordered and amorphous carbon. *Physical Review B*. Vol. 61, 2000, pp. 14095-14107.

Submitted: 22.11.2013

Accepted: 04.3.2015

Monika Madej  
Dariusz Ozimina  
Department of Tribology  
and Maintenance Materials,  
Kielce University of Technology,  
1000-lecia P.P. 7, 25-314 Kielce, Poland  
Krzysztof Kurzydłowski  
Tomasz Płociński  
Piotr Wieciński  
Department of Materials Design,  
Warsaw University of Technology,  
Wołoska 141, 02-507 Warsaw, Poland  
Michał Styp-Rekowski  
Maciej Matuszewski  
UTP University of Science and  
Technology  
Al. Prof. Kaliskiego 7, 85-796 Bydgoszcz