Journal of Machine Engineering, Vol. 12, No. 2, 2012

amorphous carbon film, DLC coating
friction, wear

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SOME OPERATIONAL FEATURES OF COATING OBTAINED WITH PACVD METHOD

The main aim of presented work was the commencing the tests and analysis of the DLC type a:C:H coatings obtained with PACVD technique on the elements from Co-Cr-Mo alloys., among others: monitoring of structure changes, hardness measurement, estimation of the surface geometrical structure and tribologic tests. The analysis of surface structure and its elementary composition were estimated with the application of scanning SEM microscope, as well as TEM transmission microscope. The hardness of the elements with and without the coating was measured with the Matsuzawa micro hardness testing tester. Tribologic test of materials wear resistance was done with using T-01M apparatus ball-on-disc type, within a set of Al_2O_3 ball – disk from Co-Cr-Mo alloys with DLC coating, in technologically dry friction condition as well as with Ringer solution lubrication. Friction tests were conducted with using tester T-17, working in association: polymer pin made of high-molecular polyethylene PE – UHMW – plate from Co-Cr-Mo alloys with DLC coating with Ringer solution lubrication.The results obtained during mentioned above tests showed that the application of DLC coatings greatly enhances the operating features of the coated surfaces.

1. INTRODUCTION

In modern science and technology, the highly important role play materials based on carbon, that can crystallize in diamond or graphite forms [1]. The diamond-like layers were discovered in 1971 by Aisenberg and Chabot who – through cooling the carbon soft ions beam in argon obtained the amorphous layers which did not contain hydrogen in their composition. The discovery became critical and initiated the transition from soft carbonic materials to the layers characterized by the high hardness, with resistance of 10^{12} Ωcm. At present, under the nickname of the diamond coating there are numerous amorphous, mostly hydrogenated, thin-layered materials with various properties, dependant on the type of the method used as well as the conditions of their obtaining. The divergence of technological systems and used technologies characterizing the obtained material leads to non-singular

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naming of them (DLC, a-DLC, a-C, a-C:H, a-C, a-D, i-C, hard carbon etc.), where the same name is used for different materials or where the similar materials are named differently. In recent years there was a significant progress both in the testing and application subject regarding the amorphous carbon. Generally, the amorphous carbon might be the mixture of the atoms with the sp^3, sp^2 or even sp^1 bonds, with the possibility of the hydrogen presence [2],[3]. Amorphous carbonic materials are characterized with high variety of structure, and their properties mainly due to the type and parameters of their production [1],[4],[5]. However, one of the important factors crucial regarding their properties is a sp^2 bonds ratio, existing in graphite for sp^3 bonds, existing in diamond's structure. Amorphous carbon with high contents of diamond sp^3 bonds is known as DLC. In Fig. 1 there are presented types of amorphous carbon in a function of concentration of hydrogen and covalence joints, as proposed by German Engineers Association VDI.

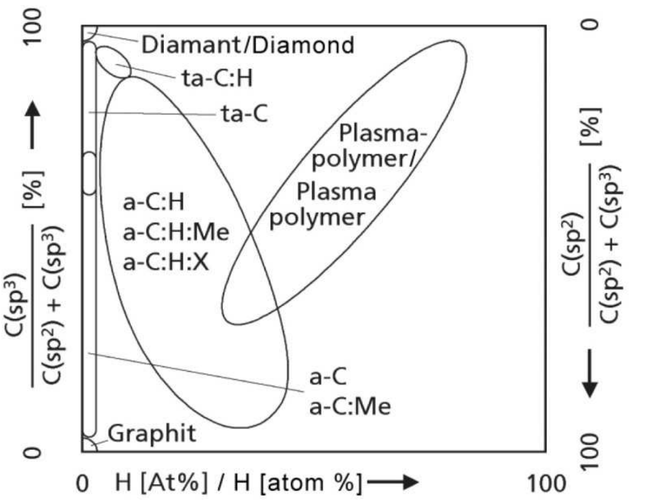


Fig. 1. Amorphous carbon types depending on the contents of sp^2 and sp^3 joints and hydrogen

Diamond as coatings a-C can be modified with metals and then they are marked as a-C:Me, on the other hand the coatings a-C:H are being modified with metals – a-C:H:Me (W, Ti, Nb, Cr, V, Co, Mo) and non-metals – a-C:H:X (H, Si, F, N, O, P, B).

Prevailing works focused on the improvement of endoprosthesis construction did not in-influence radically on the course of their wear processes. There are being applied works connected with tests regarding new materials on the friction association within those systems.

Regarding the commonly used in operating technology, the DLC coatings for the purpose of biotribological systems elements application need to fulfil definitely higher quality requirements, such as: high adhesion towards the surface, mechanical, physical and chemical stability and what is more, it is necessary that carbon atoms concentration was present with the covalence joints with sp^3 hybridization.

The following important factor that influences the structure and properties of the DLC coatings is the contents of the additional radicals. An introduction to the DLC coating of the slight amount of such radicals as H, Si, F, N, O, W, Nb, Cr, V, Co, Mo, Ti and their combination allows for keeping its amorphous character. Since the first DLC coating was obtained there was a significant development regarding the methods of their surfacing. The mentioned methods of surfacing the ultra-thin carbon layers are the most commonly used, nevertheless, it is important to add that there are quite numerous other techniques. In 2008, there were known 18 different methods of the surfacing the DLC coating. Amorphous carbon coatings are being produced with the application of various technologies of the atoms sedimentation on the surface. During the process of the DLC coating surfacing, there was used the method of the chemical sedimentation from the gas phase with the support of plasma – PACVD.

The coatings with the hydrated amorphous carbon (a-C:H) were the ones tested in the widest scope during the works regarding the biocompatibility of all of the DLC coatings.

2. EXPERIMENTAL CONDITIONS

In presented investigations there was used the Co-Cr-Mo alloy, with commercial name Biodur CCM PLUS, which chemical constitution was presented in Table 1, characterized with the high mechanical durability, corrosion resistance and the tribologic wear resistance too.

Table 1. Biodur CCM PLUS alloy chemical constitution

Chemical element	Co	Cr	Mo	N	C	Ni	Mn	Fe	Si
Contents	base	26÷30	5÷7	0,15÷0,2	0,2÷0,3	0,3	0,5	0,3	0,6

The second tested material was UHMWPE – polyethylene with very high molecular weight (2 to 10 MMg/mol) and density: 930÷944kg/m^3.

3. APPARATUS AND TESTS METHODOLOGY

During experiments following apparatus were necessary and adequate to them methodology.

The Raman Spectroscopy tests were made using the dispersion microraman spectrometer Nicolet Almega XR, with the application of the inducing line 532nm (Nd:YAG) with the power of 2,5mW. The spectrum was being recorded in a range 100÷4000cm^{-1} by the real resolution about 6cm^{-1}. The focusing of the beam was done by the application of optical microscope Olympus B51 and the lens x50. Decomposition of the spectrums were made in a Nicolet Omnic 8 program with the application of Gaussian profile.

The topography measurements AFM Atomic Forces Microscope were carried out using atomic force microscope NT-MDT company, with Smena type head in tapping mode.

There were visualized the surface topographies of the samples 50 x 50µm. Cantilever - NSG 11 of NT-MDT company possessed the following parameters:

- k = 5,5÷22,5N/m,
- resonant frequency = 223,2kHz.

In observation of the samples: Co-Cr-Mo alloy, Co-Cr-Mo alloy with the spread DLC coatings and the wear area there was used a scanning electron microscopy. The cutting-out and thinning process was carried out with the application of ionic scanning microscope (FIB) Hitachi SU 70, equipped with electron gun with the field emission of Schottki type. During the observation, the sample was inclined of the 40° angle (it was a maximal angle for this size of sample). Therefore, the surface characteristic properties (for example thickness) presented in the pictures are smaller than in reality. The actual sizes would be obtained at the angle of 90°. In the description of the results there were presented the actual dimensions, including the sample slant angle. The transmission observance was done with the use of high-resolution electron scanning microscope Hitachi s5500, equipped with electron gun with the field emission of maximum accelerating voltage 30KeV. The test was carried out in SE mod, which is the standard mod for SEM and also in STEM mod, using the beam crossing through the preparation. The tests of the chemical composition were carried out with application of energy-distributive X-ray radiation spectrometer (EDS).

The hardness tests were done with the application of microhardness tester MATSUZAWA using Vickers and Knoop intenders. The application of the latter one allows with the use of small load to eliminate the base material hardness. The tests were realized with the load of 98,07mN.

The valuable tests supplement, reflecting the character of the coatings covered elements configuration, were the measurements of the surface geometrical structure, carried out using optical profile measurement gauge Talysurf CCI of Taylor Hobson. It is a contactless profile measurement gauge using the broad-band coherence correlation interferometry. It allows to obtain high vertical resolution 0,1Å regardless of the applied magnification. The measurement's results are being recorded by the CCD camera with the resolution of 1024x1024 pixels which results in measurement having of more than a million of points of the measured surface used to generate 3D images. During the measurements the measured area was 0,33 x 0,33mm, and the measurement scope in the Z axis 2,2mm. TalyMap Platinium application made it possible to process and analyse in complex measurement data.

The tribologic tests with the application of T-01M, were carried out with the following parameters:

- friction association: ball α-Al_2O_3 – Co-Cr-Mo alloy and Co-Cr-Mo alloy with a-C:H coating,
- load P = 10N,
- slide speed v = 0,1m/s,
- friction way s = 1000m,
- relative humidity conditions – 55±5%,
- surrounding temperature T_0 = 22±1˚C.

The materials wear tests were carried out also using T-17 tester. They made it possible to estimate the friction factor character as well as the wear one and also the wear in the function of the cycles number. T-17 apparatus is designed for testing tribologic characteristics of various material associations cooperating with each other slippery in a reciprocating movement. The friction unit was the mandrel made of UHMWPE, and the disc was made of Co-Cr-Mo alloy and Co-Cr-Mo alloy with DLC coating. During the test the following quantities were measured:

- friction force,
- total linear wear of frictional joint elements,
- surrounding temperature of the friction joint and the temperature of the lubricant,
- cycles number – friction way.

The tests of metal-polymer associations were realized under the following parameters:

- test time/ number of cycles: 1.000.000 s / 1. 000. 000,
- amplitude: 12,7mm,
- frequency: 1Hz,
- average slide speed: 50mm/s,
- load: 225N,
- lubricant: RINGER reagent,
- liquid temperature during the test: 37 ±1 °C.

4. TESTS RESULTS AND THE DISCUSSION

4.1. RAMAN SPECTROSCOPY

The Raman spectroscopy provides the information regarding the atomic bonds, crystal structure and nano-crystal and amorphous carbonic systems. It consists of inelastic laser radiation photons dissipation due to the interaction with material’s atomic bonds. It causes the atomic bonds polarization oscillation change. The Raman spectrum for the most of the carbon coatings is dominated mainly by two bands located near 1500cm^{-1}. The spectrum can be resolved into two lines, the first one for about 1580cm^{-1} (peak G), and the second one for about 1350cm^{-1} (peak D). G peak is active within the monocrystal graphite and comes from the chain spatial configuration of carbon bonds with sp^2 hybridization. The disordered state increase within the graphite structure causes the occurrence of peak marked as D. It is the result of the carbon bonds with sp^2 hybridization cyclic spatial configuration occurrence. There are also being formed at the time sp^1 and sp^3 bonds. Location correlation as well as G and D peaks intensity make it possible to determine the physical properties of obtained coatings. Sometimes, there also occurs T peak, which is caused by C-C sp^3 bonds oscillations, when located about 1060 cm^{-1}, however with the activation with the laser radiation with the wave smaller than 300 nm [6]. In Fig. 2 there was presented the Raman spectrum of the obtained carbonic coatings.

The obtained Raman spectrum was resolved, with the application of Gaussian profile. In that way, there was achieved the information regarding the bands location and their intensity (I). The location of G band averages 1570cm^{-1} for the a-C:H coating, while D band 1364cm^{-1} for the a-C:H coating. In both cases the ratio ID/IG is close to 1.

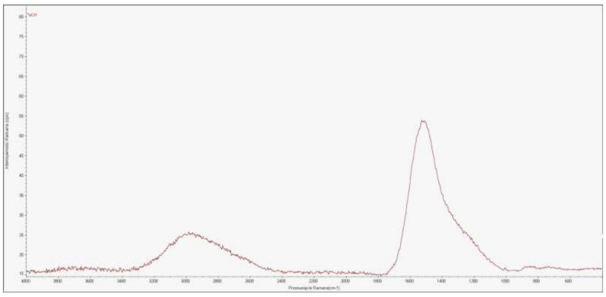


Fig. 2. Raman spectrum of the diamond-like coating

When comparing the obtained value with the data presented in [6], the content of sp^3 bonds was estimated within the presented coatings on the level of about 30%. In addition, the location of G band equals more than 1550cm^{-1} for the visible Raman spectrum activation, which also proves the high contents of sp^3 bonds within the tested coatings. What is more, the higher amplification of the Raman spectrum intensification was observed for a-C:H coating.

4.2. AFM MICROSCOPY

The test subjects were discs made of Co-Cr-Mo alloy as well as discs made of Co-Cr-Mo alloy with the DLC coatings. During the measurements with the application of atomic force microscopy (AFM) there were presented the topographic views of the Co-Cr-Mo alloy samples' surfaces and also of the Co-Cr-Mo alloy with the a-C:H coating – Fig. 3.

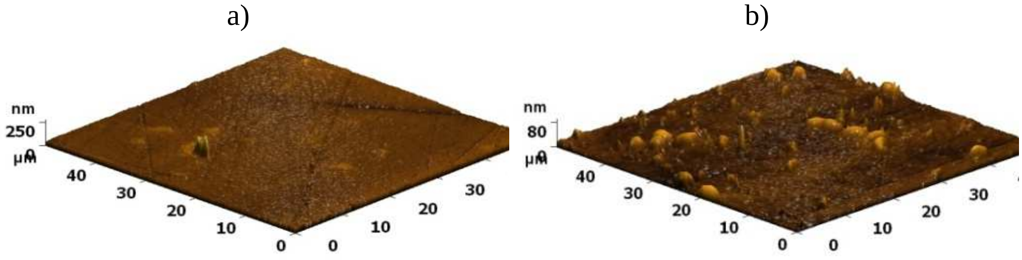


Fig. 3. AFM topography surface images of the investigated materials: a) the CoCrMo alloy; b) the DLC coating

Amongst the materials presented in above pictures, smoother surface is characterized alloy with a-C:H coating.

4.3. SCANNING MICROSCOPY (SEM) AND TRANSMISSION MICROSCOPY (TEM)

For the observation of the samples with DLC coating there was applied microscopy SEM – Fig. 4. The point microanalysis was used for the purpose of testing the elemental composition in a quantitive formula. The results of the chemical content analysis of the particular sub-coatings and the base material were presented in Figures 5 and 6 and in Tables 2 and 3.

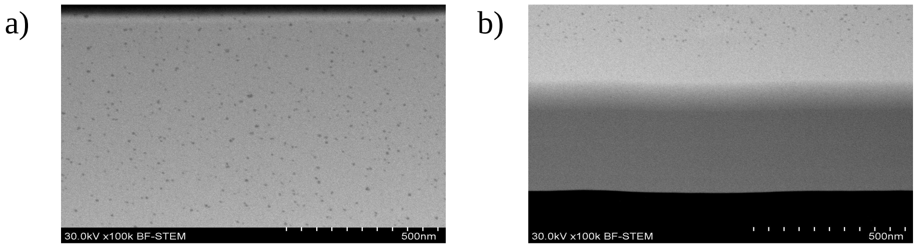


Fig. 4. Cross section of DLC coating (a), upper part of the coating and transmission layer (b) (mod: STEM)

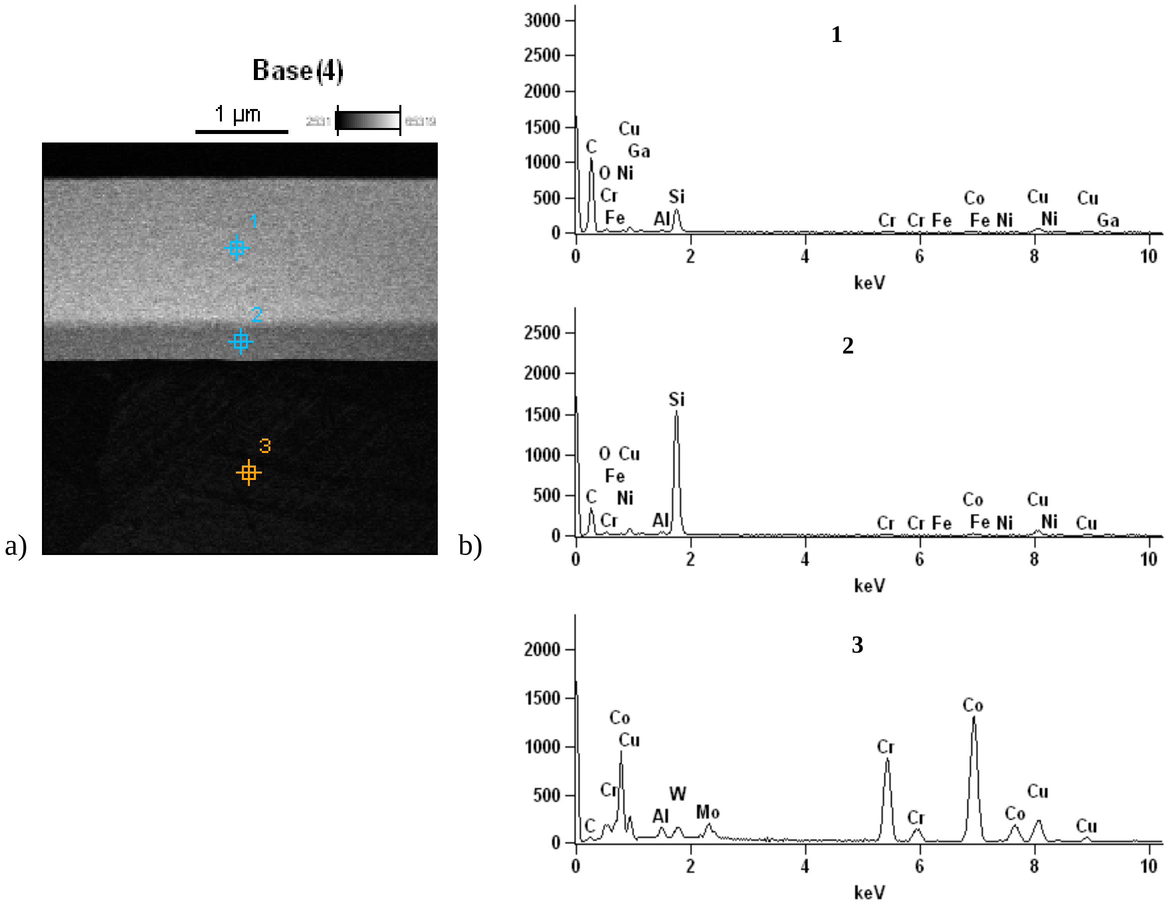


Fig. 5. The points of base and surface of chemical content analysis (a); spectrums of X-ray characteristic for particular points of chemical content analysis (b)

Table 2. Chemical constitution in atomic percent (for results presented in Fig. 5)

	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
Point 3	58.61	0.00	0.00	12.19	27.33	1.88

Table 3. Chemical constitution in atomic percent (for results presented in Fig. 6)

	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

Carbon quantitative analysis with the application of scanning electron microscope equipped with EDS is impossible. It can be even proved by the fact that the analysis showed the presence of at least 60% of C at. in a base material (Tab. 3). It is obviously impossible. Therefore, in the analysis carbon is usually not included. However, the results of this analysis allow us to form some conclusions regarding the chemical content of particular sub-coatings. The outer sub-coating is a proper DLC coating containing mainly carbon.

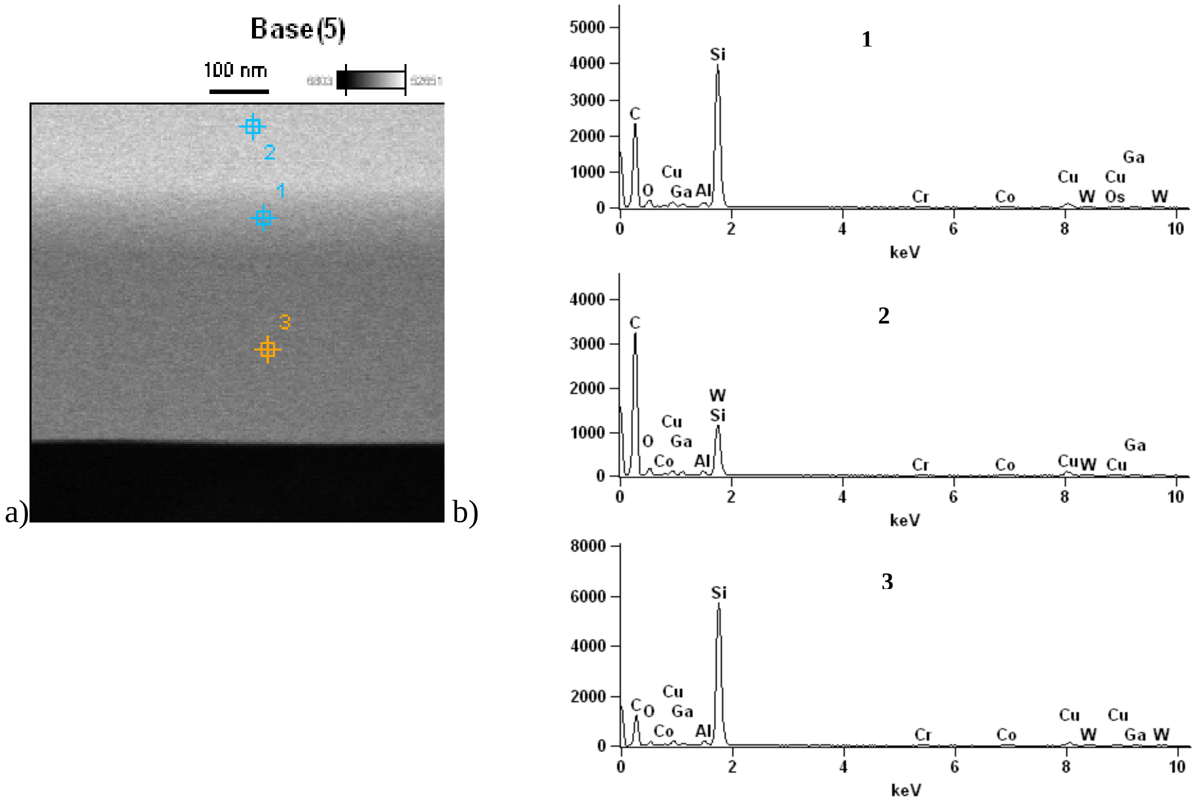


Fig. 6. The points of base and surface of chemical content analysis (a); spectrums of X-ray characteristic for particular points of chemical content analysis b)

At the same time, the sub-coating located directly on the base is a transmission coating containing mainly silicon, which was partially oxidised. The analysis without carbon demonstrated within this sub-coating the presence of 64 % Si at. and 34 % O_2 at. and also the vestigial amounts of Cr and Co. The transmission coating contains of both carbon and silicon.

4.4. MICROHARDNESS

The application of the latter one allows with the use of small load to eliminate the base material hardness. The tests were realized with the load of 98,07mN. In Fig. 7 there were compared and averaged results of 10 tested materials microhardness measured measurements.

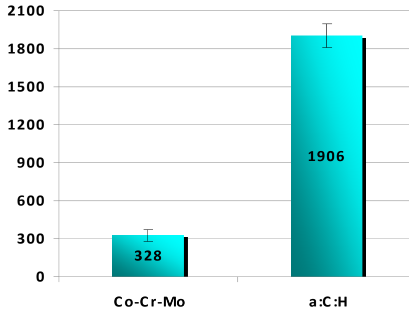
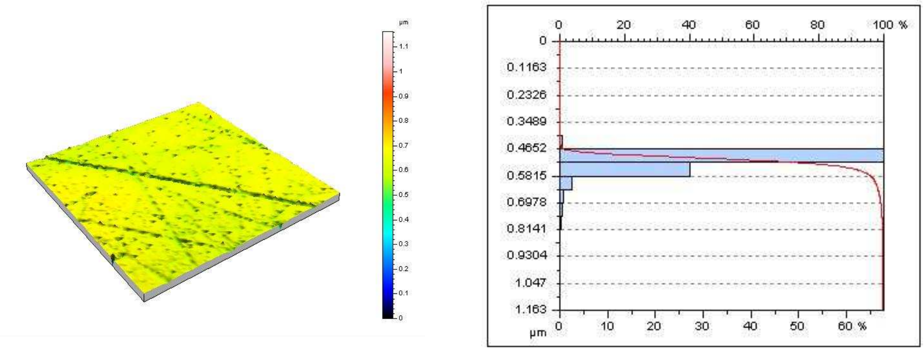


Fig. 7. Microhardness HV_{100} of tested coating materials and the base

4.5. SURFACE GEOMETRIC STRUCTURE

Images in 3D configuration and their analysis allowed for the precise study of DLC a-C:H type coating’s surface geometric structure. In Figs. 8 and 9 there are presented images of surface topography, distribution of ordinates with the load-carrying curve and the



a)

b)

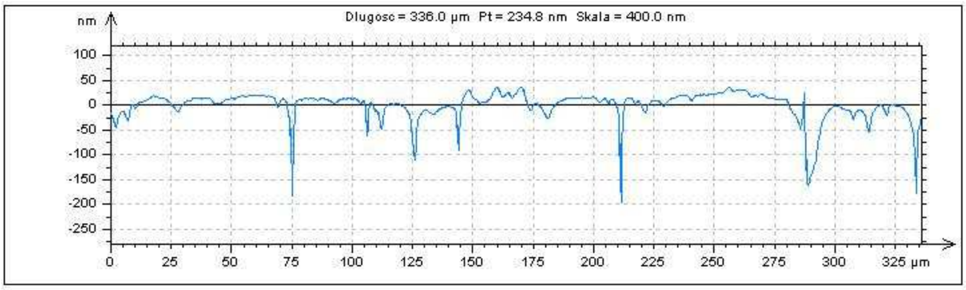
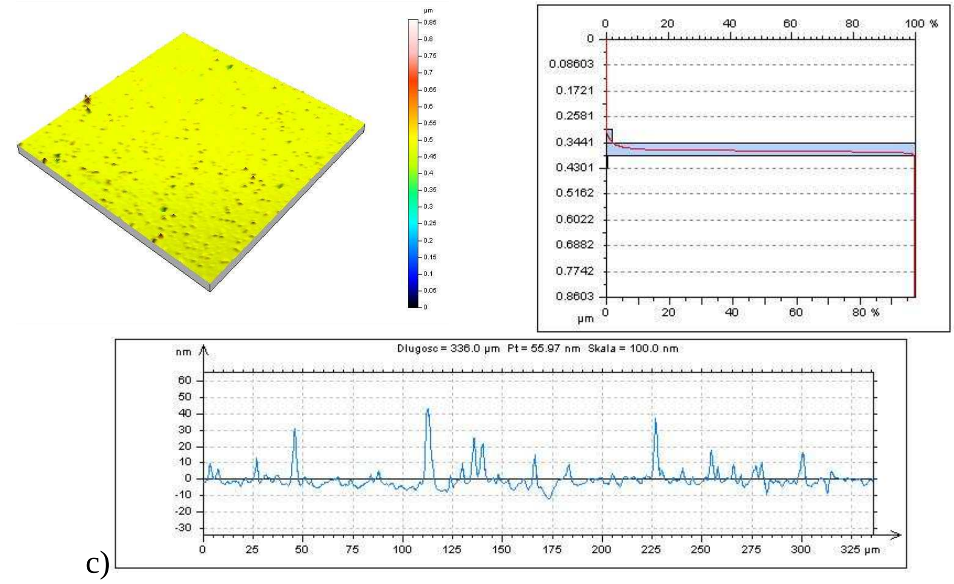

c)

Fig. 8. CoCrMo alloy geometric structure surface: a) surface topography, b) distribution of ordinates and load-carrying curves, c) surface profile


a)

b)

c)

Fig. 9. DLC type a-C:H coating's geometric structure surface: a) surface topography, b) distribution of ordinates and load-carrying curves, c) surface profile

Table 4. Surface geometric structure parameters

Parameters	**Co-Cr-Mo alloy**	**a-C:H coating**
***Sa*, µm**	0,0344	0,0048
***Sq*, µm**	0,0336	0,0120
Ssk	-1,893	-0,825
Sku	349,9	229,8
***Sp*, µm**	0,1795	0,3727
***Sv*, µm**	0,0995	0,4875
***Sz*, µm**	0,2791	0,8603

profiles of analysed ground coat and coating materials. In Table 4 there was presented the compilation of the most important parameters regarding tested samples geometric structure surface.

The bigger value of average arithmetic aberration of the *Sa* surface roughness – the basic amplitude parameter towards quantitative estimation of the analysed surface condition was recorded for the base material – Co-Cr-Mo alloy than for the a-C:H coating. The similar tendency was observed for the *Sq* surface roughness average quadruple aberration. The supplementary information regarding the forming of the tested elements surface forming provide two amplitude parameters: skewness factor – *Ssk* asymmetry and also the concentration factor – *Ssk* kurtosis. These parameters are sensitive to occurrence on the surface of local altitudes or valleys, also the defects. *Ssk* parameter in case of the both tested materials has the negative value, which indicates the plateau shaping of their surfaces. On the other hand, the obtained high values of *Ssk* are caused by the high slenderness ratio of ordinates distribution curve. In reference to the base material the DLC coating had higher values of that parameters. What is certain, the roughness of the surface influenced the tribologic properties of the materials.

4.6. TRIBOLOGIC TESTS

The results of the obtained tribologic tests with the application of T-01M tester were presented in the form of diagrams of the friction factor changes in the path function (Fig. 10) as well as the comparison of testing elements wear intensity coefficient (Tab. 5). The tests were carried out in technologically dry friction conditions and also with Ringer reagent lubrication.

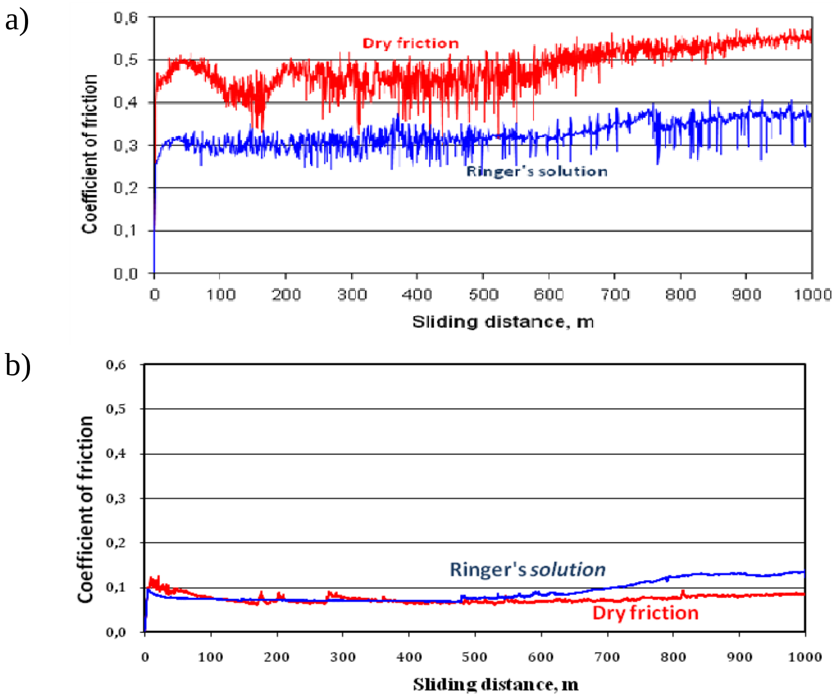


Fig. 10. Changes of friction factor in technologically dry friction conditions and also with Ringer reagent lubrication - +R in path function for: a) Co-Cr-Mo alloy, b) a-C:H coating

Table 5. The changes of wear intensity factor depending on material

Material	Wear intensity factor	
	lubrication	
	without	Ringer’s solution
CoCrMo alloy	14	6
a-C:H coating	2	4,5

Due to the carried out tests using T-01M apparatus there was ascertained that the lower friction factor was recorded for a:C:H coating. In technologically dry friction conditions, its value during the whole test evaluates in the range of 0,07÷0,09. It is also very stable in Ringer reagent lubrication condition up till nearly half of the test and it obtains the value of ~0,075. At that point it increases and after 1000 m friction way achieves the value of 0,13. In case of the analysed Co-Cr-Mo alloy the friction factor values are definitely higher and are on the level of 0,30÷0,38 in lubricating conditions and 0,48÷0,55 in technologically dry friction conditions and their run is characterized by the big value leaps. The comparison of wear intensity factor value in Table 5 shows that for the DLC coating it is definitely lower both in technologically dry friction conditions as well as limiting than for the Co-Cr-Mo alloy.

In the figures below there were presented tribologic tests results in the form of the friction coefficient μ changes (Fig. 11) in function of cycles number, and in Table 6 there were presented the mass loss of the friction bond elements.

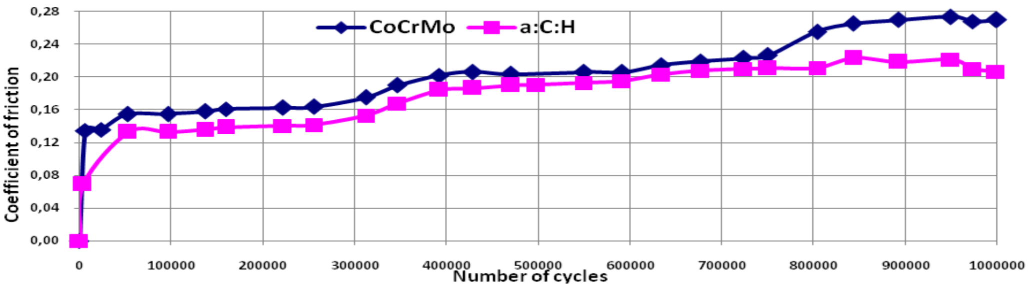


Fig.11. Diagrams of the friction coefficient changes in cycles number function for the associations: UHMWPE–Co-Cr-Mo alloy and UHMWPE–a-C:H coating

Table 6. Weight loss of the metallic-polymer friction joint

Friction element	**Specimen weight, g**		**Wear, g**
	prior to test	after test	
Co-Cr-Mo			
Plate	56,9395	56,9378	0,0017
Pin	0,6994	0,6908	0,0086
DLC			
Plate	56,9993	56,9981	0,0012
Pin	0,6998	0,6918	0,0080

During the tests using T-17 stand there was recorded lower friction factor for the a-C:H coating. From the presented diagram it is seen that after the initial, fast increase up to the value of 0,14 after about 25000 cycles it stabilizes and increases systematically reaching the value of 0,27 after 850000 cycles and maintains on this level till the end of the test. Analyzing the results, one can see that the a-C:H-type DLC coating demonstrated better tribologic properties than the base material, i.e. the Co-Cr-Mo alloy, at the same pre-determined test parameters.

5. CONCLUSIONS

The analysis carried out in the study of the presented results provides a solid justification for the authors regarding the direction of the carried out tests. The analysis of the base material – Co-Cr-Mo alloy and the DLC a-C:H type coating obtained with the PACVD method give the basis for the running the tests with the targeting on application of them as friction joints elements, including as a bio-bearings. The results of the realized tests and their analysis allow to formulate the following closing conclusions.

1. From the SEM and AFM analyses it is clear that the DLC coatings deposited by the PACVD method possessed a more homogeneous structure.
2. The AFM analysis showed decreasing of roughness parameter *Ra*, after the deposition of the DLC coating.
3. Analysis of surface geometric structure showed that the a-C:H type coating is characterized with better parameters than the base material Co-Cr-Mo alloy.
4. The values of wear rate are considerably smaller for the DLC coating than for the Co-Cr-Mo alloy.
5. In comparison with the Co-Cr-Mo alloy the tested DLC coating is characterized among other with:
   - significantly greater hardness,
   - smaller friction resistance.
6. During the tribologic tests using T-17 tester with the application of Ringer lubricant there were recorded for the a-C:H coating the lower friction factor, and its run during the whole test cycle was more stable than of alloy. There was also recorded lower total linear wear of the elements with a-C:H coating and the UHMWPE polymer in reference to the association without the coating. It was established that the mass loses of the UHMWPE mandrels after the full test cycle are lower for the association with the DLC coating than for the base material Co-Cr-Mo alloy.

The observations of the structure and analysis of the content shown the compatibility of the DLC a-C:H type coatings structure with the one assumed during the process of their production, and the Raman spectroscopy provided the information regarding the hybridized covalence joints.

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