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Diamond-like carbon coatings pin-on-disk wear testing

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The aim of this study is to evaluate the wear resistance of diamond-like carbon films and wear debris of polyethylene using pin-on-disc testing on two groups of CoCrMo discs with diamond-like carbon coatings. Diamond-like carbon coatings deposited with use high productive vacuum-arc filtered plasma source in two regimes: with and without Titanium interlayer on CoCrMo discs. The Orthopaedic Innovation Centre performed 2.5 million cycles of pin-on-disc testing on two groups of CoCrMo discs with diamond-like carbon films based on ASTM G99-17. The discs used were made of wrought low carbon alloy CoCrMo according to ASTM F1537. Wear performance of the polyethylene pins against the diamond-like carbon coated discs was determined and reported below. Lubricant samples were collected for each group after 0.5 and 2.5 million cycles of testing, and used to characterize wear particles. All polyethylene pins were assessed for damage features following 2.5 million cycles of wear testing. The damage features identified included burnishing, scratching and grooving. The new process of diamond-like carbon coating deposition from filtered vacuum arc plasma flows allows obtaining the stable diamond-like carbon coating on the CoCrMo substrate. Thus, considering the low friction coefficient and the stable behavior of diamond-like carbon such coating would be highly perspective for CoCrMo artificial joint implants.

Keywords: Diamond like carbon films, pin-on-disc test, wear debris of polyethylene, CoCrMo.

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Introduction

In recent decades, the expansion of indications for total hip arthroplasty has increased the number of younger patients who have a longer life expectancy and a more active lifestyle. the exposure of implants depends on the design and quality of the used materials. One of the ways to increase the longevity of the implant service for younger and more active patients is to reduce wear in the friction pair [1].

Wear of the polyethylene acetabular components of hip implants is a serious clinical problem. In hip arthroplasty, polyethylene wear is defined as a factor limiting the life of the implant; It is known that the formation of wear products can cause adverse tissue reactions, which can lead to a significant loss of bone mass around the implant and, as a result, to a weakening of fixation. CoCrMo metal or ceramic heads pivotally connected to ultra-high molecular weight polyethylene (UHMWPE) and metal / metal combinations form wear particles that can have adverse reactions [2]. One of the options for solving the problem of wear of friction pairs is the use of coatings that show extremely low wear in technical devices, namely, diamond-like carbon (DLC) [3].

DLC is a solid, nano-smooth, amorphous carbon material deposited on a substrate by Physical Vapor Deposition (PVD) method. DLC thin films were used due to its low coefficient of friction, high hardness, and excellent biocompatibility. Although it may have the hardness of diamond and have a high degree of bioinertness, it is non-crystalline and may contain significant concentrations of elements such as H, N and O. Many different DLC coatings have been studied as substrates for cell growth and materials for over 20 years for medical biocoatings including protective coatings for hip replacement joints, non-stick inert coatings for arterial stents and coatings for optics [4].

Due to the high internal stress of DLC these films have poor adhesion to biomedical alloys, because of the ion bombardment during deposition.

Therefore, most researchers are developing various technologies to improve diamond adhesion using intermediate layers. To date, there is no evidence in the literature for excellent adhesion of hard carbon coatings on cobalt or cobalt-chromium alloys [5].

We've used different methods to increase the adhesion to the metal base of the hip joint: metal Ti, Cr interlayer, doping DLC films by metal (Ti, Cu, Zr, etc.) or Si, N impurities, diamond nanocrystals incorporation in the DLC films and so on. The most promising method for deposition of high-quality DLC films is vacuum arc deposition. This process was performed by the vacuum arc method from a high productive source of the filtered vacuum arc carbon plasma of rectilinear type with a "magnetic island". The source was installed in a modernized installation of Bulat-6 [6-9].

The aim of the work to investigate the wear resistance of DLC films and wear debris of polyethylene using pin-on-disc (POD) testing on two groups of CoCrMo discs with diamond-like carbon coatings.

I. Material and methods

The Orthopaedic Innovation Centre (OIC) performed 2.5 million cycles (Mc) of pin-on-disc (POD) testing on two groups of CoCrMo discs with diamond-like carbon coatings (DLC) based on ASTM G99-17. The discs used were made of wrought low carbon alloy CoCrMo according to ASTM F1537. DLC coatings deposited with use high productive vacuum-arc filtered plasma source in two regimes: with and without Ti interlayer on CoCrMo discs [6-9]. Wear performance of the UHMWPE pins against the diamond-like carbon (DLC) coated discs was determined and reported below. Lubricant samples were collected for each group after 0.5 and 2.5 Mc of testing, and used to characterize wear particles. All test pins discs were divided into two groups due to the regime DLC coating deposition: group 1 – 3 discs and 3 pins, group 4 – 6 discs and 3 pins. Three additional pins were used as passive soak control samples. Wear testing was conducted using a 10x10mm square path and 3MPa constant contact pressure. Testing was conducted in bovine calf serum based lubricant.

Prior to testing, all pins and discs were marked with a unique identifier, which corresponded to their station number on the OrthoPOD. The pins were given an orientation mark which ensures consistent and repeatable placement within the pin holder.

Prior to being coated, all discs were polished to an average roughness (Ra) ≤ 20 nm. Surface roughness measurements were taken on the discs. Five roughness measurements were taken across the surface of the discs, and averaged. Measurements were taken perpendicular across the wear pattern, as shown in the Fig.1., the dashed line indicates the wear path. After the coating was applied, surface roughness measurements were taken again, as well as upon completion of testing. Five roughness measurements were taken across the surface of the discs, and averaged. Measurements were taken perpendicular across the wear pattern, as shown in the diagram below, the dashed line indicates the wear path. Digital microscope images were taken of the discs and the articulating surface of the pins. Digital photographs were taken of the articulating surfaces of the pins and discs.

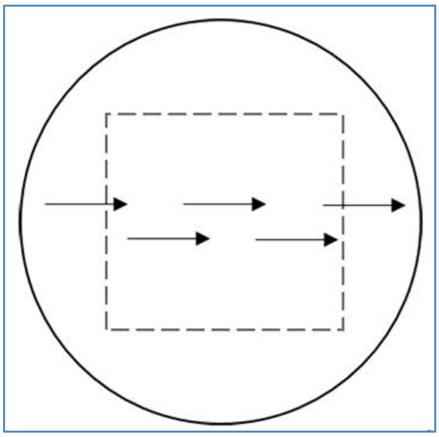

Fig. 1 Surface roughness path taken across disc.

All PE pins were cleaned and weighed to determine their dry weights. All PE pins underwent presoaking in test lubricant (bovine calf serum) at 37°C for 72 hours. All pins were removed from the lubricant and weighed according to Annex 6 in ASTM F732-17The OrthoPOD wear stations were programmed to run a 10x10 mm square under a constant 3 MPa load at 1.0 Hz. Upon completion of each interval, OrthoPOD feedback files were analyzed to ensure proper loading occurred at each station.

All pin and disc combinations were isolated in individual wells and filled with test lubricant. The test program was implemented using the loads and motions described in Table 1 and conducted for 0.5 Mc. Fluid levels were topped up daily. Following 0.5 and 2.5 Mc of testing the lubricant was collected from each individual station. Samples were combined for each group, and the container was labeled with the disc group, station numbers, collection interval and date of collection. The collected lubricant was stored in a freezer set to -25°C for particle analysis. At each 0.5 Mc interval until a total of 2.5 Mc of wear testing was completed, all pins were removed, cleaned and weighed according to the procedure outlined in ASTM F732-17. Photo documentation was taken of the articulating surface of the worn pins and discs following every test interval. Data files from the OrthoPOD were extracted and assessed to ensure proper waveforms were applied.

All station-specific wear rates, and average wear rates were determined for each test group according to Section 7 of ASTM F2025.

Following the completion of the test, qualitative analyses were performed macroscopically on all the components to determine the damage features present. Microscopic images were taken of the PE pin surface in order to characterize the damage features that were present.

Upon completion of the test, surface roughness measurements were taken of the discs, and reported.

Lubricant samples were collected after 0.5 Mc and 2.5 Mc of testing for wear particle characterization according to ASTM F1877-05. The lubricant proteins were digested, and particulate debris was isolated. Analyses involved using scanning electron microscopy (SEM) to measure particle size and shape, as well as energy dispersive X-ray analysis (EDX) to assess the elemental composition of wear particles. A minimum of 500 particles per sample were assessed. Particles were characterized by 7 distinct parameters: particle size, aspect ratio, roundness, form factor, perimeter, equivalent circle diameter, and elongation (Table 1).

OIC performed polyethylene (PE) particle analysis on wear serum collected from a pin on disc test conducted with polyethylene pins articulating against diamond-like carbon (DLC) coated discs. The OIC collected samples at the 0.5 Mc interval, and upon the completion of the 2.5 Mc interval from regime 1 and regime 2 groups. The samples were analyzed for particle characterization of PE by performing chemical digestion, filtration, imaging, and image processing. Particle characterization has been measured by aspect ratio, form factor, roundness, length (longest Feret measured), perimeter, Feret average, and equivalent circular diameter. Particles were further analyzed for elemental composition. Particle analysis complied with ASTM F561-13, ASTM F1877-16, and ISO 17853. Sample serum was digested and filtered as recommended by ASTM F561 - 13 for harvesting PE particles from wear test solutions. A 10 ml sample of vigorously shaken wear serum was added to 50 ml of 37% hydrochloric acid for chemical digestion. The solution was heated to 50 – 60°C while stirring at 350 rpm for approximately 45 minutes until protein digestion was complete. A 1 ml extraction of digested solution was added to 100 ml of methanol. Aliquots were subject to vacuum filtration through 0.1 μm polycarbonate filters. Aliquot volumes per filter analyzed was for Sample-Filter 1-A – 5 ml, for 2-A, 3-A, 4-A – 10 ml. Processed filters were sputter coated with gold. Particle imaging was executed through scanning electron microscopy (SEM). The filters were secured to an examination stage with double sided carbon tape and copper conductive tape. Image capture was taken at magnifications 100X, 500X, 1000X, and 2000X. Imaging was carried out until a minimum of 500 particles were captured for data analysis. Particle elemental composition was measured by energy dispersive spectroscopy (EDS) to confirm PE particle composition.

The images taken by SEM were analyzed for particle characterization through imaging software (Vision Lite, Clemex, Longueuil, QC, Canada). Particles were auto-detected by the software through manual grayscale thresholding and bit-plane filtering. Particle size range corresponded to magnifications recommended and modified by ASTM for particle imaging. Particle morphology was measured by the software which included: aspect ratio, form factor, roundness, length (longest Feret measured), perimeter, Feret average, and equivalent circular diameter. Data was outputted as excel spreadsheets and were used to create table data summaries and histograms.

II. Results and discussion

Surface roughness measurements were taken prior to testing, after the coating was applied, and after 2.5 Mc. Average roughness (Ra) values are averaged for each coating regime, and reported below with standard deviation (SD) - measures the amount of variability, or dispersion, from the individual data values to the mean (Table 2). The Zeiss Surfcom 2900-SD2 contact profilometer is used to perform surface roughness measurements. Specifications of this apparatus: measuring range 1000 μm, resolution 0.1 nm. The reason used this precision apparatus is confirm or refute even

Table 1.

Description of wear particle characterization parameters

Parameter	Description	Formula
Particle Size - Equivalent Circular Diameter (ECD)	Diameter of a circle with an area equivalent to the area of the particle.	$ECD = 2x\left(\frac{A}{\pi}\right)^{\frac{1}{2}}$
Aspect Ratio (AR)	Ratio of the major diameter to the minor diameter of the particle.	$AR = \frac{\text{dmajor}}{\text{dminor}}$
Roundness (R)	Resemblance of the particle to a circle.	$R = \frac{4xA}{\pi x \text{ d2max}}$
Form Factor (FF)	Similar to roundness, but based on the perimeter of the particle (roughness of particle outline).	$FF = \frac{4x\pi xA}{\text{p2}}$
Perimeter (P)	The length of the particle outline.	Determined using image-capture software
Elongation (E)	The ratio of the length to the breadth.	$E = \frac{FL}{FW}$

Table 2.

Average surface roughness measurements for the coating regimes.

	Roughness	Regime 1	Regime 2
Pre-Coating	Ra (± SD)	0.013 ± 0.003 μm	0.005 ± 0.003 μm
Coated	Ra (± SD)	0.015 ± 0.005 μm.	0.015 ± 0.005 μm
Post-Test	Ra (± SD)	0.015 ± 0.005 μm.	0.015 ± 0.003 μm

minor surface damage.

Identical roughness values were measured for discs coated with regime 1 and regime 2. After 2.5 Mc of testing, minute insignificant changes were measured in roughness values for either group, as seen in Figure 2 below.

A total of 2.5 Mc of testing was performed on PE pins and 2 types of DLC coating regimes. Each PE pin was tested with a 10 x 10mm square wear pattern. The adjusted cumulative wear for each PE pin, based on fluid absorption of the soak pins, are reported in Table 3 and Figure 3. The average wear rate for each test group are summarized in Table 3. Generally, PE pins articulating against discs coated in regime 1 showed higher cumulative and average wear, wearing an average of 1.5x higher than the regime 2 pins. Average wear rate (mg/Mc) in Regime

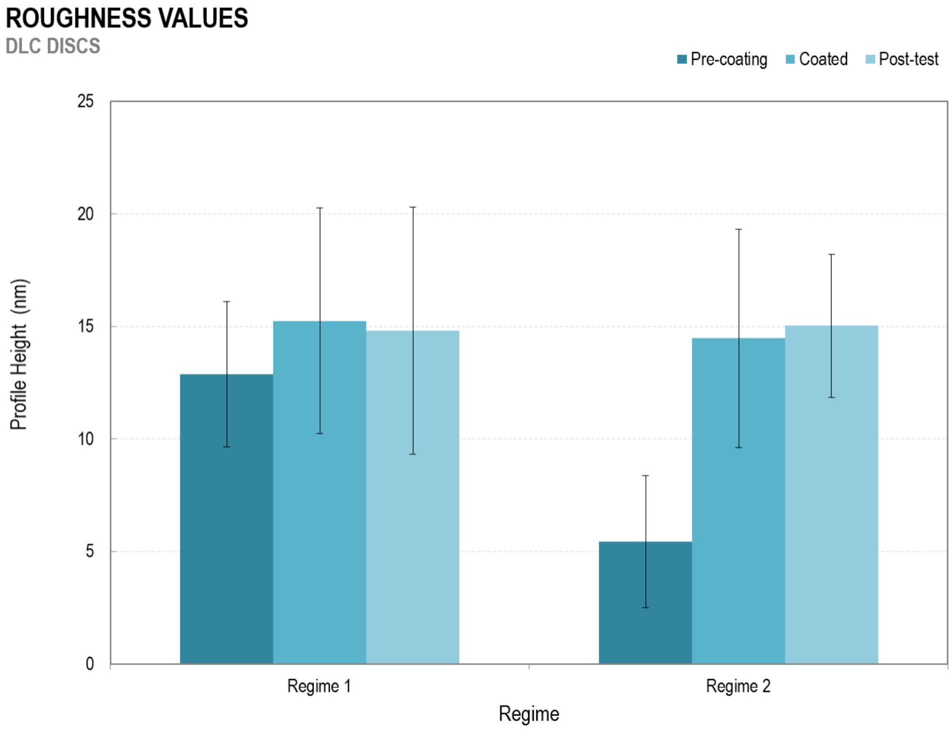

Fig.2. Roughness values for regime 1 and regime 2 discs.

Table 3.

Cumulative wear rates for PE pins after 2.5 Mc of testing.

	Regime 1			Regime 2		
	1	2	3	4	5	6
Cumulative Wear (mg)	151.964	206.394	166.857	116.031	146.584	102.558

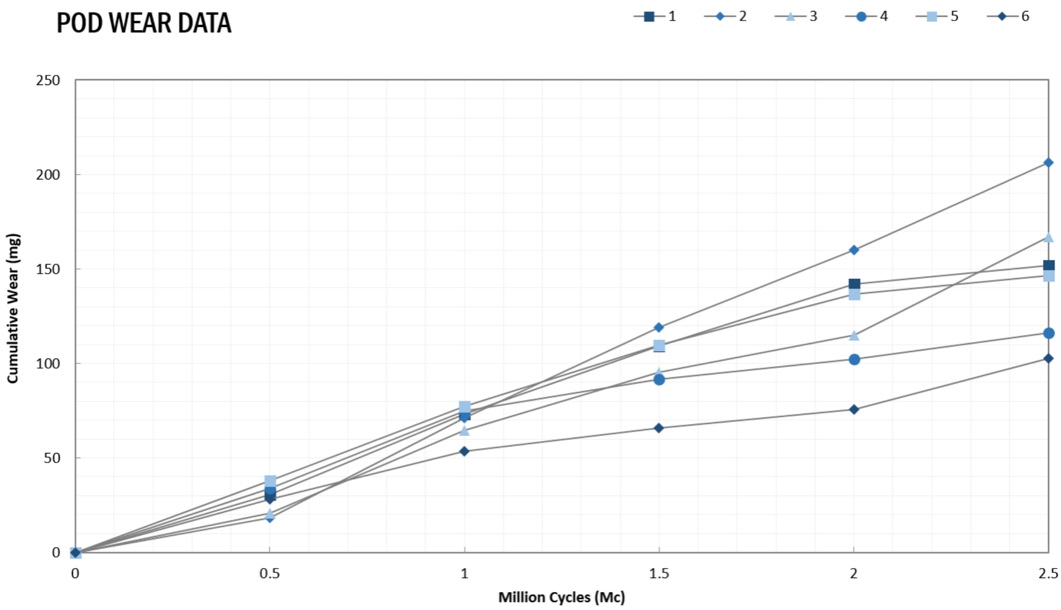

Fig.3 Cumulative wear of PE pins during 2.5 Mc POD test.

1 was 72.083 and in Regime 2 - 48.244 (Table IV).

Table 4.

Average wear rates for PE pins grouped by coating regime.

	Regime 1	Regime 2
Average Wear Rate (mg/Mc)	72.083	48.244

All PE pins were assessed for damage features following 2.5 Mc of wear testing. The damage features identified included burnishing, scratching and grooving. These features are defined as follows:

1. Burnishing: characterized by a polished, highly reflective and very smooth surface
2. Scratching: characterized by long, fine cuts within the PE surface. These cuts are directional in nature.
3. Grooving: similar to scratching, but the cuts are thicker and deeper.

Examples of these features are identified in Figure 4. Two of the pins, articulating against discs coated with different regimes had raised, round, bumps on the surface of the pins, as seen below in Figure 5. The cause of these bumps is unknown, and does not correlate to higher wearing stations.

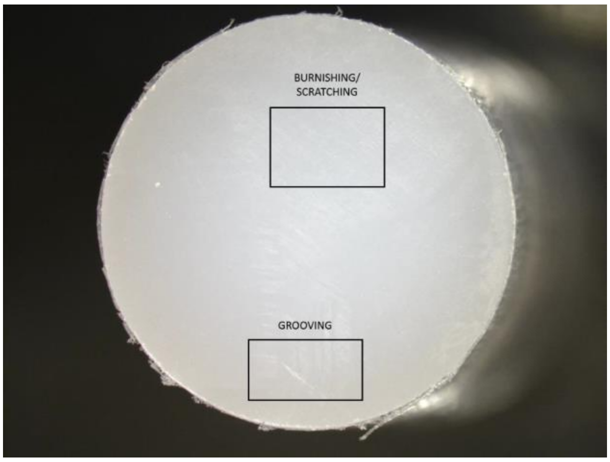

Fig. 4 Damage observed on wear station PE pin following 28 days of testing (10X magnification).

All disc materials were macroscopically assessed for damage following 2.5 Mc of wear testing. No signs of scratching or wear was seen on the surface of the discs. Figure 6 below shows all of the discs after 2.5 Mc of testing.

Wear particle characterization was performed by the OIC according to ASTM F1877-05. A summary of the results is presented in Table 5. During the run-in stage

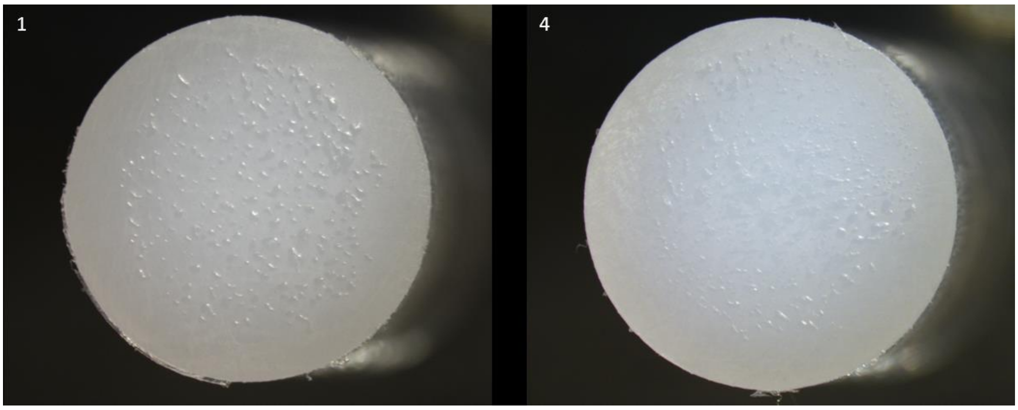

Fig. 5 Detail observed on the surface of the PE pins №1 and №4 following 2.5 Mc of testing (10X magnification).

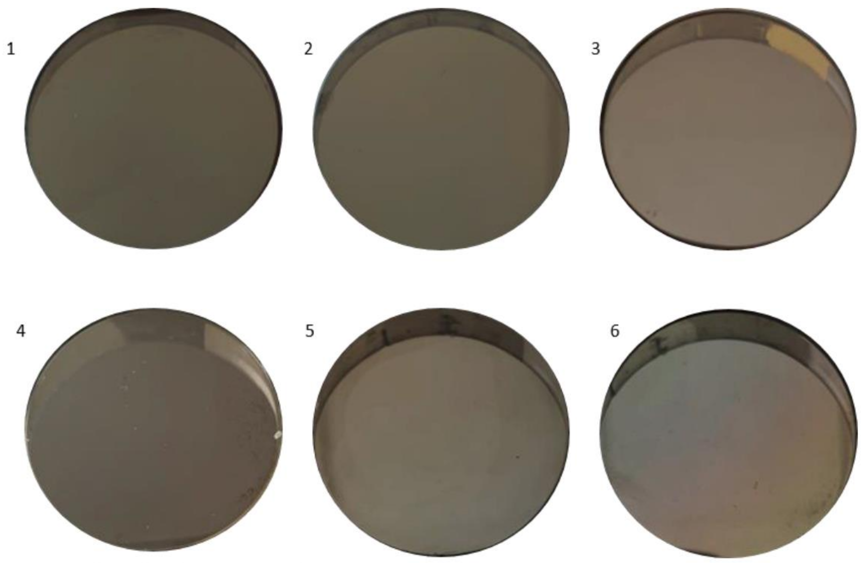

Fig. 6 Discs after 2.5 Mc of testing: CoCrMo discs number 1,2,3 with titanium interlayer under DLC after 2.5 Mc of testing; CoCrMo discs number 1,2,3 without titanium interlayer under DLC after 2.5 Mc of testing.

(0.5 Mc), larger particles were found from discs coated in regime 2 DLC, but during steady-state wear, the largest particles were in the discs coated in regime 1. The median particle length for discs coated in regime 1 at the 2.5 Mc interval were more than 2x greater than those coated in regime 2. This agrees with the higher wear seen on pins tested against regime 1 discs after 2.5 Mc of testing compared to pins articulating against regime 2 discs.

Results of polyethylene (PE) particle analysis on wear serum collected from a pin on disc test. Data summary: a total of 709, 563, 758, and 1370 particles were collected through particle analysis from samples 1, 2, 3, and 4, respectively. The mean, medial, maximum, and minimum values of particle characterization are summarized in Table 6.1 - Table 6.4. Formulas for calculating the values given in the tables 6.1-6.4 are presented in table 1.

Six PE pins underwent a total of 2.5 Mc of wear testing against DLC discs. The discs were coated using two different regimes, with pins articulating against regime 1 discs wearing significantly higher than regime 2 discs. After testing, the pins showed signs of burnishing, scratching and grooving, while the discs showed no evidence of scratching or damage. Wear particle analysis showed larger particles from samples of regime 2 discs after 0.5 Mc of testing, but during the 2.5 Mc interval, significantly larger particles were found from regime 1 stations.

Despite the introduction of new friction pairs for large joint endoprostheses, wear of the bearing surfaces of the components remains a serious problem. Wear products are known to ultimately lead to osteolysis of the bone and aseptic instability of the components of the endoprosthesis. Friction pairs ceramic-ceramic and ceramic-cross-link polyethylene showed improved wear resistance characteristics. However, due to the extreme hardness of diamond and other superhard carbon materials and the need to reduce wear on articulated implants, an active search for alternative support surfaces based on diamond-like films continues. DLC coatings have great potential for use, as they have many excellent required properties - extreme hardness, wear resistance, low friction and biocompatibility. DLC coatings can be synthesized by several methods, which lead to a wide variety of structures and properties and difficulties in comparative assessment of their tribological properties [10]. The main problem of DLC coatings, limiting the use of large joints in friction pairs, is the problem with residual stress; a higher sp^3 content results in a harder coating, but due to the higher compressive stress, the internal compressive stress in DLC coatings can reach 10 GPa, which sharply limits the coating thickness. Such stresses can create unstable interfaces, in other words, problems with adhesion arise, which leads to the fact that the diamond-like film can become prone to delaminating [11].

Therefore, most researchers are developing various technologies to improve DLC adhesion using intermediate layers. To date, there is no evidence in the literature for excellent adhesion of hard DLC coatings on cobalt or cobalt-chromium alloys [10]. To improve the adhesion of DLC coatings, titanium substrates are used either from pure titanium or its Ti6Al4V alloy due to the formation of tightly bound interfacial titanium carbide. For example, the authors have demonstrated exceptional adhesion of diamond coating while maintaining very low surface roughness and ultra-high hardness on Ti-6Al-4V substrates synthesized by microwave plasma CVD with a feed gas consisting of a high methane content (15 vol%) [12]. Comparing data from different studies is difficult due to different coating technologies, different test operating conditions, and different sizes of discs and polyethylene.

For example, Haider H. et al. note that the contact area between pin and disk is the most important factor affecting the rate of wear of polyethylene, and this fact is consistent with clinical results [13]. An important characteristic is also the time elapsed since the synthesis of polyethylene and the conditions of its storage.

Besong and his colleagues tested UHMWPE pins made from components that had been stored for a long time and found that gamma irradiation in air followed by prolonged aging (up to 10 years), as well as the roughness of the flat surface of the disc, had a strong effect on the wear rate [14].

Other authors note that the radiation dose of polyethylene, which indicates the level of crosslinking of

Table 5.

Summary of wear particle characterization following 0.5 Mc and 2.5 Mc of wear testing.

	0.5 Mc Collection Run-In Wear		2.5 Mc Collection Steady State Wear	
	Regime 1	Regime 2	Regime 1	Regime 2
Median Feret Diameter (μm) [range]	0.33 [0.16 – 18.27]	0.60 [0.16 – 20.27]	0.61 [0.18 – 26.10]	0.40 [0.20 – 26.68]
Median Length (μm) [range]	0.38 [0.20 – 85.88]	0.69 [0.20 – 55.42]	1.02 [0.20 – 196.70]	0.48 [0.23 – 33.95]
Median Aspect Ratio [range]	1.39 [1.06 – 3.10]	1.43 [1.09 – 2.70]	1.42 [1.10 – 2.75]	1.50 [1.08 – 3.04]
Median Roundness [range]	0.63 [0.29 – 0.88]	0.63 [0.28 – 0.85]	0.66 [0.28 – 0.84]	0.67 [0.32 – 0.93]
Median Form Factor [range]	0.83 [0.52 – 0.93]	0.83 [0.53 – 0.94]	0.85 [0.50 – 0.95]	0.88 [0.60 – 0.96]
Median Perimeter (μm) [range]	0.99 [0.42 – 54.73]	1.66 [0.45 – 65.37]	1.81 [0.41 – 85.14]	1.05 [0.47 – 93.08]
Median Equivalent Circle Diameter (μm) [range]	0.29 [0.12 – 15.64]	0.54 [0.14 – 17.77]	0.56 [0.15 – 18.51]	0.37 [0.19 – 22.31]

Table 6.1.

Summary of particle characterization from sample 1 – 0.5 Mc collection, regime 1 discs.

	Aspect Ratio	Form Factor	Roundness	Length (μm)	Perimeter (μm)	Feret Average (μm)	Equivalent Circle Diameter (μm)
Mean	1.45	0.82	0.62	1.87	1.59	0.54	0.49
Median	1.39	0.83	0.63	0.38	0.99	0.33	0.29
Max	3.10	0.93	0.88	85.88	54.73	18.27	15.64
Min	1.06	0.52	0.29	0.20	0.42	0.16	0.12

Table 6.2.

Summary of particle characterization from sample 2 - 0.5 Mc collection, regime 2 discs.

	Aspect Ratio	Form Factor	Roundness	Length (μm)	Perimeter (μm)	Feret Average (μm)	Equivalent Circle Diameter (μm)
Mean	1.49	0.82	0.62	1.88	4.55	1.55	1.41
Median	1.43	0.83	0.63	0.69	1.66	0.60	0.54
Max	2.70	0.94	0.85	55.42	65.37	20.27	17.77
Min	1.09	0.53	0.28	0.20	0.45	0.16	0.14

Table 6.3.

Summary of particle characterization from sample 3 - 2.5 Mc collection, regime 1 discs.

	Aspect Ratio	Form Factor	Roundness	Length (μm)	Perimeter (μm)	Feret Average (μm)	Equivalent Circle Diameter (μm)
Mean	1.46	0.84	0.65	22.70	2.86	0.96	0.87
Median	1.42	0.85	0.66	1.02	1.81	0.61	0.56
Max	2.75	0.95	0.84	96.70	85.14	26.10	18.51
Min	1.10	0.50	0.28	0.20	0.41	0.18	0.15

Table 6.4.

Summary of particle characterization from sample 4 – 2.5 Mc collection, regime 2 discs.

	Aspect Ratio	Form Factor	Roundness	Length (μm)	Perimeter (μm)	Feret Average (μm)	Equivalent Circle Diameter (μm)
Mean	1.50	0.87	0.66	0.64	1.41	0.53	0.49
Median	1.50	0.88	0.67	0.48	1.05	0.40	0.37
Max	3.04	0.96	0.93	33.95	93.08	26.68	22.31
Min	1.08	0.60	0.32	0.23	0.47	0.20	0.19

molecules, is an important parameter, followed by normal load, average surface roughness of the disc, shape factor of the wear path (i.e. lateral shear), test duration and sliding distance over cycle [15].

In one study, hydrogen-free amorphous DLC films were deposited at low temperatures by physical vapor deposition on medical grade CoCrMo and Ti6Al4V titanium alloy. Mechanical characteristics included measurement of surface roughness, contact angle, adhesion and wear, biocompatibility was assessed by osteoblast attachment (OB) and cell viability using live / dead analysis. The authors demonstrated reduced wear of DLC coatings and superior in vitro cyto compatibility compared to CoCrMo and Ti6Al4V implant materials without coating [16,17]. Using the method of filtered pulsed plasma in the discharge mode, the authors deposited DLC coatings to stainless steel alloys AISI316L, Ti6A14V, and CoCrMo (80% sp^3 bonding, 0.2 to 10 μm thick). Tribological studies using the post-on-disc device with coated or uncoated implant materials show that in all combinations studied, the DLC coating definitely improved wear and corrosion resistance compared to uncoated materials [18]. In vitro tribological studies using DLC-coated implants have shown that due to the different types of DLC and test conditions used [19, 20].

In another study, wear on the hinge surfaces of the hip joint was reduced to almost negligible by the use of DLC coatings deposited by the pulsed plasma arc method. The wear rate determined on a hip simulator for 15 million walking cycles (corresponding to approximately 15 years of clinical use) with serum lubrication was 1,000,000 times lower than for conventional polyethylene-metal friction pairs [21, 22]. The DLC acts as a solid lubricant, turning into graphite where it creates a transfer layer so it causes a light slip between the contact surfaces. A significant reduction in friction and wear rate is achieved through the use of a combination of DLC-coated micro-cavities on a Ti-6Al-4V substrate [23-25].

Choudhury D. and colleagues studied the durability of Ti6Al4V titanium alloy with a DLC coating under edge loading conditions for use in hip arthroplasty. Multilayer DLC coatings consist of three main layers, each of which has been designed for specific functions, such as increasing fracture toughness, adapting to stress and increasing wear resistance. The durability test used a ball-on-disc multidirectional wear tester. Surface hardness, modulus of elasticity and Raman intensity were measured prior to the wear test. The results showed a significant reduction in wear on DLC coated Ti-6Al-4V discs compared to uncoated Ti-6Al-4V discs. It is noteworthy that similar silicon nitride (Si_3N_4) balls also gave a reduced specific wear rate when rubbed against coated discs.

Therefore, the combination of functional multi-layer DLC and Si_3N_4 could be a potential candidate for prosthetic implants that will perform a longer life cycle against edge load induced wear [26]. Six types of DLC coatings with zirconium (Zr) -containing interlayers on a titanium alloy (Ti-6Al-4V) have been investigated to improve the biotribological performance of orthopedic implants. The coatings consist of three layers: above the substrate, a set of layers of 32 alternating Zr and ZrN (Zr: ZrN) sublayers, followed by a Zr and DLC (Zr: DLC) layer, and finally a nitrogen doped DLC layer. Biotribological experiments were carried out in simulated body fluid using ball-to-disc contact with a Si_3N_4 ball and rotational-vibrational motion to simulate hip movement in terms of gait angle, dynamic contact pressure, velocity and body temperature.

The results showed that the Zr: DLC layer has a significant effect on removing DLC delamination from substrates. The DLC/Si_3N_4 pairs significantly reduced the coefficient of friction, squeaking noise and wear on both Si_3N_4 balls and discs compared to Ti-6Al-4V/Si_3N_4 pairs after being tested for a duration equivalent to one year of natural hip movement [27]. A possible use case is a pairing of DLC versus DLC friction. In the spinal disc implant simulator, the DLC-DLC hinge showed no significant wear up to 100 million cycles, which corresponds to approximately 100 years of in vivo use [28]. Thus, films of diamond-like carbon (DLC), obtained by the improved technology of deposition a Ti6Al4V titanium alloy substrate, can be used as a coating of wear surfaces of friction pairs due to its hardness, low friction, low wear, and high corrosion resistance [29].

Conclusion

Investigation of wear resistance of DLC films and wear debris of polyethylene using pin-on-disc (POD) testing on two groups of CoCrMo discs with DLC coatings have been performed. DLC coatings deposited with use high productive vacuum-arc filtered plasma source in two regimes: with and without Ti interlayer. Pin-on-Disc test showed signs of burnishing, scratching and grooving on polyethylene and average wear rate (mg/Mc) in regime 1 was 72.083 mg/Mc and in regime 2 – 48.244 mg/Mc. Wear particle analysis showed larger particles from samples of regime 2 discs after 0.5 Mc of testing, but during the 2.5 Mc interval, significantly larger particles were found from regime 1 stations. DLC coatings showed no evidence of scratching, damage or delamination from the CoCrMo discs. The novelty of the research is developing and practical testing the new process of DLC coating deposited from filtered vacuum arc plasma flows allows obtaining the stable DLC coating on the cobalt chromium-molybdenum substrate. Thus, practical value of this investigation is the new step to covering CoCrMo artificial joint implants considering the low friction coefficient and the stable behavior of such DLC films.

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Conflict of interest:
The authors of this paper have no financial or personal relationships with other people or organizations that could inappropriately influence (bias) our study.

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[1] PW Grieco, S Pascal, JM Newman, et al. *New alternate bearing surfaces in total hip arthroplasty: A review of the current literature*. J Clin Orthop Trauma, 9(1), 7 (2018); https://doi.org/10.1016/j.jcot.2017.10.013.
[2] MT Manley, K Sutton, *Bearings of the future for total hip arthroplasty*, J Arthroplasty, 23(7 Suppl): Epub 2008 Aug 12. PMID: 18701242, 47 (2008 Oct); https://doi.org/10.1016/j.arth.2008.06.008.
[3] K Bewilogua, D Hofmann, *History of diamond-like carbon films-From first experiments to worldwide applications*, Surf Coat Tech., 242, 214 (2014); https://doi.org/10.1016/j.surfcoat.2014.01.031.
[4] R Hauert, K Thorwarth, G Thorwarth, *An overview on diamond-like carbon coatings in medical applications*, Surf. Coat. Technol. 233, 119(2013.); https://doi.org/10.1016/j.surfcoat.2013.04.015.

[5] SA Catledge, R Vaid, P 4th Diggins, JJ Weimer, M Koopman, YK Vohra, *Improved adhesion of ultra-hard carbon films on cobalt-chromium orthopaedic implant alloy*, J Mater Sci Mater Med. 2011 Feb;22(2), 307-16. Epub 2011 Jan 8. PMID: 21221739; PMCID: PMC3078568; https://doi.org/10.1007/s10856-010-4207-1.
[6] V.V. Vasylyev, A.A. Luchaninov, *Strel'nitskij, V.E. High-productive source of the cathodic vacuum-arc plasma with the rectilinear filter*, Problems of Atomic Science and Technology,"Vacuum, pure materials, superconductors». 89(1), 1 (2014).
[7] V.V. Vasylyev, A.A. Luchaninov, V.E. Strel'nitskij, *Deposition of the diamond-like coatings on the surfaces of the ring-shaped dry gaseous seals made of SiC for use in high pressure compressors*, Problems of Atomic Science and Technology,. "Vacuum, pure materials, superconductors», 111(1), 88 (2018) (In Russian).
[8] Ukrainian patent 97584 C23C 14/35 (2006.01). Method and device for transporting vacuum arc plasma with filtration from macroparticles // Vasylyev V. V., Strel'nitskij V. E.; assignee: National Science Center "Kharkov Institute of Physics and Technology" – № a 2010 13230; Date: 08.11.2010; Date of Patent: 27.02.2012, Bul. № 4 (in Russian).
[9] USA Patent # US 9,035,552 B2, Method and Device for Transporting Vacuum Arc Plasma // Vasylyev V. V., Strel'nitskij V. E.; assignee: National Science Center «Kharkov Institute of Physics and Technology» – No. PCT/UA2011/000105; Date: 04.08. 2013; Date of Patent: 05.19.2015.
[10] S.A. Catledge, V. Thomas, & Y.K. Vohra, *Nanostructured diamond coatings for orthopaedic applications*. Woodhead publishing series in biomaterials, 105 (2013); https://doi.org/10.1533/9780857093516.2.105.
[11] F.Platon, P. Fournier, S. Rouxel, *Tribological behaviour of DLC coatings compared to different materials used in hip joint prostheses*, Wear 250(1-12), 227 (October 2001); https://doi.org/10.1016/S0043-1648(01)00651-2.
[12] H Haider, D Baykal, *Wear Assessment of UHMWPE with Pin-on-Disc Testing*, UHMWPE Biomater. Handb, Elsevier; 553 (2016); https://doi.org/10.1016/B978-0-323-35401-1.00030-2.
[13] AA Besong, JL Hailey, E Ingham, M Stone, BM Wroblewski, J Fisher, *A study of the combined effects of shelf ageing following irradiation in air and counterface roughness on the wear of UHMWPE*, Bio-Medical Materials and Engineering, 7(1), 59 (1997).
[14] A. Borjali, K. Monson, & B. Raeymaekers, *Predicting the polyethylene wear rate in pin-on-disc experiments in the context of prosthetic hip implants: deriving a data-driven model using machine learning methods*, Tribology international, 133, 101 (2019); https://doi.org/10.1016/j.triboint.2019.01.014].
[15] C Hinüber, C Kleemann, RJ Friederichs, L Haubold, HJ Scheibe, T Schuelke, C Boehlert, MJ Baumann, *Biocompatibility and mechanical properties of diamond-like coatings on cobalt-chromium-molybdenum steel and titanium-aluminum-vanadium biomedical alloys*, J Biomed Mater Res A, 95(2), 388 (2010), PMID:20648536; https://doi.org/10.1002/jbm.a.32851.
[16] RK Roy, KR Lee, *Biomedical applications of diamond-like carbon coatings: a review*, J Biomed Mater Res B Appl Biomater, 83 (1):72 (2007) PMID: 17285609; https://doi.org/10.1002/jbm.b.30768.
[17] R Lappalainen, A Anttila, H Heinonen, Diamond coated total hip replacements. Clin Orthop Relat Res. 1998 Jul;(352):118-27. PMID: 9678039.
[18] R Hauert, *A review of modified DLC coatings for biological applications*. Diam Relat Mater., 12 (3), 583 (2003).
[19] R Hauert, K Thorwarth, G Thorwarth. An overview on diamond-like carbon coatings in medical applications. Surf Coat Tech. 233 (SupplementC):119 (2013).
[20] R Lappalainen, M Selenius, A Anttila, YT Konttinen, SS Santavirta, *Reduction of wear in total hip replacement prostheses by amorphous diamond coatings*. J Biomed Mater Res B Appl Biomater., 66(1), 410-3 (2003 Jul 15), PMID: 12808601; https://doi.org/10.1002/jbm.b.10026.
[21] S Santavirta, *Compatibility of the totally replaced hip. Reduction of wear by amorphous diamond coating*. Acta Orthop Scand Suppl., 74(310):1 (2003 D), PMID: 14768485; https://doi.org/10.1080/00016470310018108.
[22] S Ghosh, D Choudhury, T Roy, A Bin Mamat, HH Masjuki, B Pingguan-Murphy, *Tribological investigation of diamond-like carbon coated micro-dimpled surface under bovine serum and osteoarthritis oriented synovial fluid*, Sci Technol Adv Mater., 16(3), 035002 (2015); https://doi.org/10.1088/1468-6996/16/3/035002.
[23] D Choudhury, H Ay Ching, AB Mamat, J Cizek, NA Abu Osman, M Vrbka, M Hartl, I Krupka, *Fabrication and characterization of DLC coated microdimples on hip prosthesis heads*, J Biomed Mater Res B Appl Biomater. Jul;103(5), 1002 (2015); https://doi.org/10.1002/jbm.b.33274.
[24] D Choudhury, F Urban, M Vrbka, M Hartl, I Krupka, *A novel tribological study on DLC-coated micro-dimpled orthopedics implant interface*. J Mech Behav Biomed Mater., 45, 121 (2015); https://doi.org/10.1016/j.jmbbm.2014.11.028.
[25] D Choudhury, JM Lackner, L Major, T Morita, Y Sawae, A Bin Mamat, I Stavness, CK Roy, I Krupka, *Improved wear resistance of functional diamond like carbon coated Ti-6Al-4V alloys in an edge loading conditions*, J Mech Behav Biomed Mater., 59, 586 (2016); https://doi.org/10.1016/j.jmbbm.2016.04.004.
[26] D Choudhury, J Lackner, RA Fleming, J Goss, J Chen, M Zou, *Diamond-like carbon coatings with zirconium-containing interlayers for orthopedic implants*, J Mech Behav Biomed Mater., 68, 51 (2017); https://doi.org/10.1016/j.jmbbm.2017.01.023.
[27] K Thorwarth, G Thorwarth, R Figi, et al., *On interlayer stability and high-cycle simulator performance of diamond-like carbon layers for articulating joint replacements*. Int J Mol Sci., 15(6), 10527 (2014).

[28] Schultz et al., Mat-wiss u Werkstofftech 2004; 35: 924-928; Lappalainen et el., J Biomed Mater Res B Appl Biomater, 66B, 410-413 (2003); Tiainen, Diam Relat Mater, 10, 153-160 (2001).
[29] Allen et al., J Biomed Mater Res B Appl Biomater 2001; 58: 319-328; Uzumaki et al., Diam Relat Mater, 15, 982-988 (2006); Hauert, Diam Relat Mater, 12, 583-589 (2003); Grill, Diam Relat Mater, 12, 166-170 (2003).

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Випробування на зношення алмазоподібного вуглецевого покриття

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Мета цього дослідження полягає в дослідженні зносостійкості алмазоподібних вуглецевих (АПВ) плівок і уламків зносу поліетилену за допомогою випробування штифтом на диску на двох групах дисків CoCrMo з АПВ покриттями. АПВ покриття, нанесені з використанням високопродуктивного джерела плазми з вакуумно-дуговим фільтром у двох режимах: з прошарком Ti та без нього на дисках CoCrMo. Центр Ортопедичних Інновацій виконав 2,5 мільйона циклів (Мц) тестування POD на двох групах дисків CoCrMo з АПВ на основі ASTM G99-17. Використані диски були виготовлені з кованого низьковуглецевого сплаву CoCrMo відповідно до ASTM F1537. Нижче було визначено показники зносу поліетиленових штифтів проти дисків з АПВ покриттям. Зразки мастильних матеріалів були зібрані для кожної групи після 0,5 і 2,5 Мц тестування та використані для визначення характеристик частинок зносу. Після випробувань на знос тривалістю 2,5 Мц усі штирі поліетилену були оцінені на ознаки пошкодження. Виявлені ознаки пошкодження включали полірування, подряпини та канавки. Новий процес осадження АПВ покриття з фільтрованих потоків вакуумно-дугової плазми дозволяє отримати стабільне АПВ покриття на підкладці CoCrMo. Таким чином, враховуючи низький коефіцієнт тертя та стабільну поведінку АПВ, таке покриття буде дуже перспективним для імплантатів штучних суглобів CoCrMo.

Ключові слова: алмазоподібні вуглецеві плівки, тест pin-on-disc, знос поліетилену.