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A novel functional layered diamond like carbon coating for orthopedics applications

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ABSTRACT

Functional Layered "Diamond like Carbon (DLC)" coated interfaces for orthopedic load bearing applications were fabricated and assessed. They consisted of three layers, each designed for specific functions. The fabrication process was performed using magnetron sputtering at low temperatures on steel substrates. Structural investigations showed the layers possessed very fine grained, columnar microstructures with a very low density of inter columnar micro-cracks. The mechanical and surface properties such as micro hardness, wettability, roughness, modulus of elasticity, water contact angle and absorbed protein layer (γ-globulin) varied among the DLCs. The biotribological tests, conducted under simulated hip joint conditions (friction, wear, Raman intensity ratio and polyethylene wear debris) were correlated with their surface and material properties. The DLC (sample no #ML1), which were built with 0.6 μm thick tribological layer (a-C:H:Cr–a-C:16 bilayers, ratio: 1:1) and 0.15 μm thin (a-C:H) top layer was found to yield superior tribological performances at "DLC on Polyethylene" sliding pairs. On the other hand, DLC (sample no#GL3), which consist of 0.6 μm thick tribological layer (gradient layer a-C:H > a-C:N) and 0.15 μm thin (a-C:H) top layer was found to yield finest tribological performances at "DLC on DLC" sliding pairs.

1. Introduction

Diamond like carbon (DLC) has the potential to be coated onto orthopedic implant interfaces because of its excellent mechanical and tribological properties including hardness, high wear resistance and biocompatibility [1–3]. The drawbacks are low adhesion strength, poor toughness and higher residual stress [4,5]. Synovial fluid is a corrosive fluid containing a high concentration of ionic species, as well as organic and biological molecules that are capable of forming complexes with metallic species accelerating corrosion [6]. Since DLC is a porous material, a number of nano/μ size pinholes may exist and the synovial fluid can penetrate the substrate [4]. The majority of commercially available wear resistant coatings consist of one or two hard layers with high sensitivity to through-thickness fracture [7]; the placement of softer layers in between harder ones may arrest crack propagation at internal interfaces by energy dissipation and crack deflection [8,9]. The improved toughness of such coatings would be related to the nano-scale shearing of the harder layers on the softer (inter-) layers, preventing the build-up of high-bending stresses [9,10]. Such a material combination can simultaneously increase hardness and reduce the intrinsic growth stresses, resulting in markedly improved wear resistance [11,12]. A number of attempts have been carried out to address these issues. For example, interlayers such as titanium (Ti) [13], chromium carbide (Cr_3C_2) [13], and silicon nitride (Si3N4) [5] are known to reduce residual stress, thus improving adhesion. The interlayers usually enhance corrosion resistance, by offering a physical barrier between the substrate and body fluid [4]. Additionally, materials such as silver (Ag), nitrogen(N), fluorine (F) and titanium (Ti) are doped into DLC for reducing the residual stresses without compromising the wear and corrosion resistance [1,14,15]. Despite of these advancements, an optimization has not achieved yet, especially in their long-term in vivo

Abbreviations: a-C, amorphous carbon; a-C: H, hydrogenated amorphous carbon (a-C:H); UHWMPE, ultra-high-molecular-weight polyethylene; a-C:H:Cr, chromium doped hydrogenated amorphous carbon (a-C:H); a-C:H:Ti, titanium doped hydrogenated amorphous carbon (a-C:H); a-C:N, nitrogen doped amorphous carbon; Ta-C, tetrahedral amorphous carbon; SD, standard deviation.

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success of orthopedic implants. According to Love et al. [1], most DLC oriented biotribology studies do not contain details of the coating and its interlayer properties. The ideal DLC coating should have a balance modulus of elasticity and hardness relationship in the interface of coatings and substrate, and this relationship can be achieved by multilayered structures [16]. Therefore the fabricated DLC will have generally higher resistance to cohesive and adhesive crack propagation compared to single layered coating types [7,17]. DLC coatings with a combination of hardness, flexibility (lower elasticity) and toughness are potential candidates for orthopedics applications where minimal wear and ion release is important [16].

Friction, wear and lubrication of an interface can be influence by many parameters including surface roughness, wettability, hardness and modulus of elasticity and their adhesion behaviors with the contacting interfaces [18,19]. Therefore, measurements of these properties can help predict in vivo tribology. In our previous review articles [2,20], it was concluded that the experimental parameters utilized in friction and wear were widely diverse, including the choice of lubricant, thus their outcomes are difficult to compare. Moreover, to measure wear analysis of hard and ultra-thin coatings, such as DLC is extremely difficult and inconsistence, in that case, advanced measuring technique such as Raman spectroscopy is an ideal option in detecting any morphological changes of the rubbed interface due to tribo-corrosion [21].

This work focuses on nine types of functional DLC coatings on AISI 5210 steel. Prior to tribological testing, the mechanical properties (hardness and modulus of elasticity), surface properties (Roughness and wettability) and absorbed protein film (γ-globulin) were determined. Tribology testing was performed at a medium walking gait in presence of simulated body fluid and water. Tribological outcomes were endorsed with friction and wear data, and consider the presence of resultant debris. Finally, Raman signal analysis was considered for selecting the optimum coating for orthopedic interface applications.

2. Methods

The methods are classified into three groups: (a) state of art of coatings and their morphological characteristics (b) the material and surfaces properties of the DLC coated surfaces and (c) tribological investigations and their outcomes.

2.1. State of art of coatings and their morphological characteristics

Before the deposition started, the substrates (steel) were cleaned ultrasonically by ethanol and dried. After mounting on the substrate carousel, the vacuum chamber was pumped down to the start pressure for deposition (2×10^{-3} Pa). Plasma etching by an anode layer ion source (ALS) [22] was applied to remove any micrometer sized contamination and to chemically activate the composite surface in an oxygen atmosphere. Unbalanced magnetron sputtering in an industrially-scaled, 4 rectangular cathode vacuum chamber was chosen to deposit Cr, Cr_2N, a-C:H:Cr, and a-C:H coatings from high purity chromium (99.99%, RHP Technology GmbH, Seibersdorf, Austria) and electrographite carbon targets (99.9%, Schunk Group, Bad Goisern, Austria), respectively. Few of the samples were doped with Titanium (Ti) and Nitrogen (N); Table 1 shows the details protocol for N doped DLC coated substrates.

The following coating architectures were developed based on former works [16,23,24]. There are a total of nine types of DLCs fabricated in this study and all have three defined layers: a) load support layer, b) tribological functional layer and c) tribological top layer. These three layers are expected to distribute generated stresses gradually throughout interfaces and help the coating to survive longer. The load support layer consist of a 2.5 μm thick 'Cr-Cr_2N multilayer (2:1 ratio), which is same to all of the experimental DLC. Different amount of bilayers were used in multilayer deposition (8,16) with different thickness ratio of a-C:H:Cr/ a-C (1:1, 2:1, 4:1). The gradient layers were designed by linearly increasing or decreasing sputter power and gas flow: sputter power on carbon targets is generally increasing starting from 0, while the power on chromium targets decreases to 0. The C_2H_2 gas flow always finalizes at the end of tribological function layer deposition with 0, while the N2 gas flow always increases from 0 at the beginning. Hereby, we used the variation, that the N_2 flow starts either at the beginning of deposition of this layer or after 1/3 of thickness (0.2 μm). Similarly, the top layer consist of either a:C-H or a:C with a variable thickness. The details of the coating thickness and their chemical composition can be found in the Table 2.

2.2. Mechanical and surface analysis

Material and surface properties of a sliding interface are key factors influencing tribological performance and durability [18], thus it is crucial to characterize these properties before any tribological testing [25]. Roughness and information of bulges [26,27], hardness and modulus of elasticity, water contact angle and absorbed globulin film thickness [28] were evaluated in this study. Surface topography including roughness and bulges was evaluated using a Broker Atomic Force Microscopy and a 3D Color Laser Microscope (VK-9700 K). Each of the samples was measured at least five times by using a 10 and 20 magnifying lenses. Hardness and modulus of elasticity of the coated and non-coated surfaces were carried out by using a nano-indenter (DUH-211/DUH-211S Dynamic Ultra Hardness Tester, Shimadzu, Japan). The instrument is capable of measuring dynamic indentation depth on very thin films and post-treated surface layers that are impossible to measure with conventional methods [29]. The 20 mN load was applied at a speed 0.66 mN/s with a holding period of 15 s. Five repeated readings were taken for each of the samples. To measure the water contact angle, a contact angle analyzer (OCA15EC, Dataphysics Instruments, Germany) was used. In total, five readings were carried out for each specimen.

Absorbed film thickness of Globulin was measured by using a Spectroscopic Ellipsometry (Horiba Jobin Yuon™) [30]. Ellipsometry is an optical technique that measures changes in the reflectance and phase difference between the parallel (R_P) and perpendicular (R_S) components of a polarized light beam upon reflection from a surface [31]. In

Table 1
Details of coating protocol for nitrogen doped and without nitrogen doped DLC.

Coating protocol for GL3							
Step	Cr Power (W)	C Power [W]	C_2H_2 [sccm]	Ar [sccm]	N_2 [sccm]	Time [min]	
1	1400	50	5	45	0	14	1/3
2	1230	410	4.4	45.6	0	14	
3	1060	780	3.8	46.2	0	14	
4	890	1150	3.1	45.2	1.7	14	2/3
5	720	1520	2.5	44.2	3.3	14	
6	550	1890	1.9	43.1	5.0	14	
7	380	2260	1.3	42	6.7	14	
8	210	2630	0.6	41.1	8.3	14	
9	50	3000	0	40	10.0	14	

Coating protocol for GL5					
Step	Cr Power (W)	C Power (W)	C_2H_2 [sccm]	Ar [sccm]	Time [min]
1	1400	50	5	45.0	14
2	1230	410	4.4	45.6	14
3	1060	780	3.8	46.2	14
4	890	1150	3.1	46.9	14
5	720	1520	2.5	47.5	14
6	550	1890	1.9	48.1	14
7	380	2260	1.3	48.7	14
8	210	2630	0.6	49.4	14
9	50	3000	0	50.0	14