Review

Effects of surface coating on reducing friction and wear of orthopaedic implants

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Received 22 July 2013
Accepted for publication 10 September 2013
Published 7 January 2014

Abstract
Coatings such as diamond-like carbon (DLC) and titanium nitride (TiN) are employed in joint implants due to their excellent tribological properties. Recently, graphite-like carbon (GLC) and tantalum (Ta) have been proven to have good potential as coating as they possess mechanical properties similar to bones—high hardness and high flexibility. The purpose of this systematic literature review is to summarize the coating techniques of these four materials in order to compare their mechanical properties and tribological outcomes. Eighteen studies published between January 2000 and February 2013 have met the inclusion criteria for this review. Details of their fabrication parameters, material and mechanical properties along with the tribological outcomes, such as friction and wear rate, were identified and are presented in a systematic way. Although experiment conditions varied, we conclude that Ta has the lowest wear rate compared to DLC, GLC and TiN because it has a lower wear rate with high contact pressure as well as higher hardness to elasticity ratio. However, a further tribology test is needed in an environment which replicates artificial joints to confirm the acceptability of these findings.

Keywords: surface coating, artificial joints, friction, wear

1. Introduction
Hip or knee replacement is now a common surgical procedure with a very high success rate. It is significant in the treatment of severe arthritis. Implantation of artificial joints reduces the pain and improves the function and quality of life of patients. Currently, artificial joints only last 10–15 years before failing by aseptic loosening due to periprosthetic osteolysis. The root cause of osteolysis has been traced to the body’s response with the presence of polyethylene (PE) wear debris, which is one of the articulating bearing surfaces. Therefore, a reduction of wear at the rubbing interface of the joint is required. Studies have been done with an aim to improve artificial joints reliability and durability to prevent osteolysis. Highly wear-resistant and biocompatible bearing surfaces can lower debris generation in the artificial joints. Most prostheses are made of a metallic component articulating against polymer or ceramic-on-polymer. The metallic components are usually cobalt–chromium–molybdenum (CoCrMo) and titanium alloys (Ti–6Al–4 V) whereas the polymer component is ultrahigh molecular weight PE (UHMWPE). The ceramic materials are made of alumina or alumina–zirconia.
There are number of parameters affecting the wear of contacting components in artificial joints such as the patient’s level of activities, body weight, quality and quantity of synovial fluid, the level and type of stresses on the articulating surfaces, material properties, geometry and dimension, imperfections of the components and surgical techniques and accuracy. Excellent tribo-corrosion performance, low toxicity to the body and healthy interactions with the cells in the body render in a safe growth surface in artificial joints. Coating materials inserted into the body interact with the synovial fluid and its protein components. Protein adsorption arises with the nature of the physiological conditions and affinities of the surface. The type of proteins absorbed to the surface and their conformation will govern the cellular response.

A plausible approach to enhance the durability of artificial joints is to engineer the bearing surfaces with a highly wear-resistant coating. The smoother the articulating surface, the less wear will occur. The relation of coating surface in biomedical applications is substantial in determining the success of a hip or knee implant. Coatings improve the surface properties including the hardness, wettability, elastic strain, friction coefficient and wear of hip and knee prostheses. Coating materials used in joints replacement are fabricated by physical [1, 2] or chemical vapour deposition (CVD) [3, 4], electrodeposition [5], thermal treatment in molten salts [6, 7], laser shaping [8, 9] and ion implantation [10, 11]. In this review, we evaluate the friction and wear performance of different coating materials including diamond-like carbon (DLC), graphite-like carbon (GLC), tantalum (Ta) and titanium nitride (TiN). We kept our search limited to last 13 years since the methodology of biotribology experiments has improved a lot during this period and we focus on recent development of coating materials. Wear of the ceramic materials is substantially (two orders of magnitude) lesser than that of PE, and the wear of the carbon coating is several times lesser than that of the ceramic materials.

**2. Methodology**

The selection criteria for this systematic review are journal papers written in English with experimental works published between January 2000 and February 2013. ‘Surface coating’, ‘artificial joints’, ‘wear’ and ‘friction’ were the main keywords used for searching Web of Science, Science Direct, SpringerLink and PubMed. There were a total of 1018 papers found from the databases. The title and abstract of the papers were reviewed extensively to ensure relevance of the topic. Only 18 papers were selected in accordance with the inclusion and exclusion criteria, as shown in figure 1.

**Inclusion criteria.** Studies that focus on the tribological effect of various types of coating materials including DLC, Ta, GLC and TiN.

**Exclusion criteria.** Papers that are related to mathematical modelling, finite element analysis, antimicrobial properties, corrosion behaviour, tissue engineering and biological effect in animals are excluded. Clinical surveys and review papers are also removed from the study.

**3. Results**

**3.1. Overview of coating**

Coatings are normally used to improve the surface properties of the substrate without changing the bulk materials [12]. Moreover, coatings can act as an effective barrier to minimize the release of ions attributing to tribo-corrosion [13–15]. It can increase the hardness along with excellent surface finishing, thus reducing the friction and wear rate [1, 16, 17]. However, one limitation of coatings is their adhesion to the substrate allowing the interactions of chemical bonds between the layers. Moreover, their abilities in cyclic loading condition are still being researched. It is necessary to define coating dimensions (thickness, hardness and surface finish) which have an ability to protect the substrate from the excessive wear (abrasive, fatigue and corrosive) and to provide a low friction transferring film on the opposing surface. This review focuses on four main types of coatings which are Ta, GLC, DLC and TiN. DLC and TiN have been used in many orthopaedic applications [18]. GLC possess both hardness and flexibility [19]. Porous Ta is found to have a similar material structure to bone [20, 21].

Ta is a biocompatible metal and it possesses excellent corrosion resistance with low ion release. It is also suitable in the coating of implant surface among most of the materials used in hip or knee implants such as stainless steel, ceramic, cobalt–chromium and titanium alloys. Balagna et al [6] presented the work on Ta-rich coating deposited on cobalt–chromium–molybdenum (CoCrMo) alloys through a thermal treatment in molten salts. Ta coating with thickness less than 1 µm is a suitable implant for the substitution of joints owning to its good wear resistance. The surface
roughness demonstrated a moderate increment considered acceptable for the ultimate purpose. Ta is a new metallic biomaterial which has been shown to be bioactive and can biologically bond to the bones. Trabecular Ta exhibits excellent scaffolds for bones in growth and mechanical attachment. Scaffolds, which are made of 99 wt% pure Ta and 1 wt% glass carbon, are implanted as acetabular caps or scaffolds for bone reconstruction [22]. Recent studies have shown that Ta coatings exhibit excellent cellular adhesion. This is attributed to the wettability characteristic of its structure. Ta surface has lower contact angles and higher surface energy and is therefore able to improve cell–material interactions [23].

The newly developed GLC is a hydrogen-free, amorphous and carbon–chromium coating which possesses hexagonal layer lattice. GLC could be used in many existing applications such as valves, seals and washers. GLC coatings are being tested for use in artificial hip joints and they have been shown to present no biocompatibility problems. The uncoated hip joints are claimed to have a useful life in excess of 10 years whereas the GLC coated joints with coating thickness of 2 µm are likely to have a lifetime of up to 50 years. It is thought that GLC can be applied in knees and other joints [24].

DLC is a carbon-based coating composed of diamond (sp³) and graphite (sp²) bonds. A high sp³/sp² ratio leads to diamond-like properties. DLC coatings can be prepared by physical vapour deposition (PVD) or CVD processes from a variety of solid or gaseous carbon sources. The superior hardness and toughness of the carbon allotrope diamond has gained attention in biomedical implant applications. Most of the DLC coatings deposited on alloy steels endure poor levels of adhesion, high intrinsic stresses and low load bearing capability. Taeger et al [25] reported that DLC coated femoral heads reveal detrimental results within 8.5 years of following up with DLC patients. This was attributed to the inadequate adhesion of the coating. The DLC coatings chipped off over time, causing a considerable increase in wear and implant failure. The ability to modify the DLC coating surface by doping and changing the compositional variation is an added advantage in improving the coating characteristics. Research on functional graded materials [8] or titanium ion-implants [26] has been done to improve the adhesion of DLC coatings. DLC coatings are excellent in both bio and hemocompatibility [5]. The double bonds in the carbon react with reactive oxygen and remove the superoxide radicals, whereby the radicals can cause tissue damage, including strokes and cancers [27].

Nanocrystalline diamond (NCD) is another type of diamond-based material where the grain size ranges from 3 to ~100 nm. NCD coatings have isotropic tribological properties and can be deposited on substrates with complex shape [28]. NCD is formed by the decomposition of methane in a process of radio frequency (RF) plasma activated vapour deposition. Wear properties of ultra smooth nanostructured diamond (UNSD) deposited using microwave plasma CVD (MPCVD) had better wear performance against PE compared to CoCrMo [17]. NCD forms a diffusion barrier between the implant and human environment; the diamond layers are biocompatible with living organism [29].

TiN was first introduced back in the 1980s for ceramic coating of artificial hip and knee replacements [30]. TiN coating in golden colour is normally deposited by PVD or laser deposition. Tribological testing showed a very good wear rate for TiN against PE. In addition, it exhibits an increase in hardness and a decrease in metal ion release from the substrate [31, 32]. The ceramic layer reduces the release of metal ions into the patient’s joint space and minimizes bacterial proliferation [33]. In the 1990s, TiN coatings have successfully been applied to shield the body surface from metal ions that could cause allergic reactions [34]. Adhesion resistance of TiN coating on the softer metal was a serious drawback, which was believed to be the result of third body abrasive wear from bone cement particles. High stresses created from the contact with hard particles trapped between the two articulating surfaces (acetabular and femoral head), subsequently resulted in coating breakthrough in the femoral heads [2]. Delamination and corrosion occurred through the pinhole of the substrate due to hard third-body wear [35]. Many researchers have raised concerns about the ability of TiN coatings to withstand wear damage in clinical applications. Table 1 illustrates the advantages and disadvantages of different coating materials.

Most of the total knee joints consist of a metal femoral component made from a CoCrMo alloy and a tibial component with a UHMWPE-bearing surface. CoCrMo has excellent mechanical properties; high corrosion and wear resistance, rendering a wide usage in joint prostheses [36]. However, the corrosion rate of CoCrMo devices is increased due to human body fluids and surface friction. The excess of Co and Cr content causes hypersensitivity and drastic inflammatory reactions. The toxicity of Co and Cr is dependent on its valence state, concentration and exposure time. Cr(III) can cause chromosome breakage and DNA damage [37, 38].

PE particles in the surrounding tissue are associated with osteolysis leading to loosening and failure. Wear resistance of PE improves with increased cross linking of the polymer chains. However, it may change the amorphous and crystalline regions of the resulting polymer, affecting the mechanical properties and fatigue characteristics. Cross linked PE works well in hip designs and its application in knee replacement is still under consideration [39].

Ti–6Al–4 V has long been a main medical titanium alloy used in implant applications. The alloy exhibits low shear strength and low wear resistance when used in an orthopaedic prosthesis. However, the alloy has a possible toxic effect resulting from the release of vanadium and aluminium. The Young’s modulus between titanium implants (103–120 GPa) and bones (10–30 GPa) have a vast discrepancy, which is unfavourable for bone healing and remodelling [40]. Titanium alloys are corrosion-resistant and inert biomaterials. Ceramic-based materials are widely used in orthopaedic implants; however, their main drawback is brittleness under impact loads [41].

Figure 2 represents the percentage of papers selected for coating materials. DLC is the most frequently used
Table 1. Advantages and disadvantages of coating materials.

| Materials | Advantages                                              | Disadvantages                                      |
|-----------|---------------------------------------------------------|----------------------------------------------------|
| Ta        | Low ion release [6]                                     |                                                    |
|           | High corrosion resistance [6]                           |                                                    |
|           | Low toxicity [7]                                        |                                                    |
|           | High biocompatibility [6, 7, 77]                         |                                                    |
|           | Higher wettability [7]                                  |                                                    |
| GLC       | Moderate hardness [1]                                   | Hardness is lower than for DLC [1]                 |
|           | Wear resistance [1]                                     |                                                    |
|           | Lower friction than DLC [24]                            |                                                    |
|           | High load-bearing capacity [1]                           |                                                    |
|           | Good adhesion [24]                                      |                                                    |
| DLC       | Hard [3]                                                | Brittle [24]                                       |
|           | Low friction [5]                                        | Poor adhesion [10, 24]                              |
|           | High wear [5]                                           |                                                    |
|           | Corrosion resistance [79]                               | High internal stress upto 10 GPa or more [8, 24]   |
|           | Chemical inertness [3, 5, 10]                            |                                                    |
|           | High electrical resistance [5]                          |                                                    |
|           | Optical transparency [5]                                |                                                    |
|           | Biocompatible [3, 10, 11]                               |                                                    |
|           | High electrical resistivity [43]                         |                                                    |
| TiN       | Hard [9]                                                | Hard, can enhance wear by abrasion of the opposing surface [2] |
|           | Wear resistant [9]                                      |                                                    |
|           | Low price [70]                                          |                                                    |
|           | Corrosion resistance [5]                                |                                                    |

Figure 2. Different types of coating materials used in the selected papers.

coating materials (61%) in artificial joints due to their superior tribological properties. Ta and GLCs are not widely known within the orthopaedic industry, but a few studies showed their potentiality for use in joint prostheses. TiN is a surface-coating technology with over 10 years of clinical history [42].

3.2. Coating deposition methods

For many years it has been possible to deposit a wide range of hard and wear resistance coatings on substrates using either chemical deposition or physical deposition. The deposition process is very dependent on the degree of flexibility in terms of the substrates and coating materials [43]. The ideal fabrication process is one which can give good quality such as a dense, homogeneous coated surface and excellent adhesion to the substrate. The deposition parameters play a crucial role in defining the film properties. Figure 3 presents the coating methods used in the papers selected for the review.

PVD consists of the generation of plasma metal ions that are transported by an electric field to the surface to
be coated. The physical deposition method has the ability to vary the deposition parameters over a wide range. The components forming the film are charged with high energies and deposited on a substrate with particular structural and thermal states [44]. The method can be used to deposit almost any type of inorganic material as well as some kinds of organic materials. PVD coatings are more corrosion resistant than coatings applied by the electroplating process. However, a high capital cost is required with a large amount of heat dissipated in cooling systems. The rate of deposition is usually quite slow [45]. Nanocomposite films with enhanced adhesion to Ti–6Al–4V alloy substrates were successfully deposited by one of the physical deposition methods called pulsed laser deposition [8]. The laser surface modification technique offers a high range of process controllability and flexibility. The advantages of the laser surfacing technique include chemical cleanliness, distortion, controlled thermal penetration and the ease to automate [46].

CVD is the process of a chemically reacting volatile compound of a material to be deposited. Reaction occurs when other gases or condensation of a compound from the gas phase onto substrate to form a solid deposit. Highly pure materials with structural control at the atomic or nanometre scale can be produced using CVD at low processing temperatures. CVD has the capability for producing coatings of complex shape engineering components and the fabrication of nano-devices and ceramic matrix composites [47].

The methods and parameters for depositing the coating materials on different types of substrates are listed in table 2. Balagna et al [6] studied the properties of coated materials at 970 and 990 °C. Ta-enrichment was found to be greater at 970 °C than 990 °C. Furthermore, coating quality was lower at the shorter time, 30 min, and corrosion occurred at the longer time, 60 min. The ideal time frame for the coating process was 45 min because it had the maximum weight increment.

Spriano et al [7] focused on a Biodur alloy due to its arthroprosthesis application. The heat treatment at 1000 °C for 60 min was chosen because it is close to the annealing temperature employed for the Biodur alloy. He observed that Co-120-800 (120 min at 800 °C) sample showed a deeper wear track than the Co-60-800 (60 min at 800 °C) alloy. So it can be concluded that a longer thermal treatment is not encouraged in getting a well adherent and thick surface modification layer. A significant Ta surface enrichment with a thickness of approximately 3 µm, on the Biodur alloy can be obtained with a temperature of 1000 °C. The coating showed a diffusion interface, continuous and well adherent. The use of higher coating temperature that leads to some diffusion bonding or an interlayer may improve the coating characteristics.

Fox et al deposited graphite-like coating with a low friction, high hardness, high load capacity and exceptionally low wear on silicon using a magnetron sputter ion plating system [14]. Three carbon targets and one chromium target were used to produce chromium carbide (CrC)–C multi-layer coating with a thickness of 2.5 µm, and the deposition process was carried out at less than 250 °C. Chromium was included in the graphite coating to make it less brittle and to show a higher load-bearing capacity. The coatings were electrically conducted and the bonding was almost entirely sp2; there was no significant diamond content detected [24]. GLC films with a titanium concentration of about 3.0 at.% were successfully deposited on silicon wafer substrates using an unbalanced magnetron sputtering system with different bias voltages. Four targets were used with A and B targets (graphite, purity 99.99%), C (graphite/titanium) and D (titanium, purity 99.99%) to produce three layers graphite-like coating containing carbon film as the top layer, titanium carbide in the interlayer and the bottom pure titanium layer. A base pressure of 10−3 Pa was reached with the deposition system heated up to 100−120 °C [1].

The process of electron cyclotron resonance (ECR)-MPCVD enabled a high production rate of plasma species, low substrate temperature and independent control of ion energy during the depositions [3]. DLC with a bigger surface area can be easily deposited using CVD at wide range temperatures (0−400 °C). However, DLC has a temperature dependence in both service and deposition. Higher wear and friction obtained with deposition took place at an elevated temperature (> 200 °C). DLC coating using ion beam conversion produced elemental sulphur, fluorine or nitrogen and thus resulted in lower friction [10].

A schematic diagram to deposit DLC on Ti–6Al–4 V substrate is shown in figure 4. The Ti–6Al–4 V alloy has been widely used as an artificial joint for its low modulus, high specific strength and superior corrosion resistance [10]. The low friction coefficient of DLC coatings can be attributed to the partial graphite sp2-bonded structure [48]. Hydrogenated DLC (DLCH) consists of amorphous carbon with a significant fraction of C–C sp3 bonds and H content in the 20−40 at.% range [49]. DLCH layers with a thickness in the range of 250−700 nm were deposited on pristine (V) and gamma irradiated (I) substrates. The deposition used acetylene, Ar and H2 as gas mixture with applied bias voltage of 200 V. DLCH coatings on metallic components have been developed to reduce the wear rate and corrosion of metallic components in artificial knee and hip joints. Figure 5 illustrates the pulsed laser deposition system in coating the functionally gradient DLC–silver nanocomposite (FGAg1) and the functionally gradient DLC–titanium (FGTi2). DLC on silicon (100) formed a silicon carbide interfacial layer, and DLC on Ti–6Al–4 V formed a titanium carbide interfacial layer. The silicon carbide interfacial layer appeared to provide better DLC film adhesion than the titanium carbide interfacial layer. This result suggests the importance of interfacial bonding in promoting adhesion of a DLC film to a given substrate [8].

3.3. Mechanical properties of coating

The nature of the coating materials with different mechanical properties and surface morphology are presented in table 3. In a joint implant, the stress level depends on the gait and the contact area between articulating tibial and femoral components (knee implant), acetabular and femoral components (hip implant) [50]. If the coated surface has high roughness, it will result in abrasion and rapid wear of the opposing surface [51].
Table 2. Coating deposition methods.

| Coating Material | Substrate | Deposition method | Deposition parameter | Equipment | Thickness (µm) |
|------------------|-----------|-------------------|----------------------|-----------|---------------|
| Ta [6]           | CoCrMo (D = 30 mm, t = 3 mm) | Thermal treatment in molten salts | T = 950–1000°C | Tubular furnace under argon flux | < 1 |
| Ta [7]           | Pure cobalt and cobalt micro-melt alloy (Biodur) | Thermal treatment in molten salts | Time = 30–60 min, T = 800–1000°C | Furnace with argon flux | 3 |
| GLC [24]         | Si        | Magnetron sputtering | Time = 60–120 min, T = < 250°C | Teer coatings uniform deposition and plasma magnetron sputter ion plating system | 2.5 |
| GLC–TiC– Ti [1]  | Silicon wafer | Magnetron sputtering | T = 100–120°C | Unbalanced magnetron sputter | 1.6 |
| GLC–TiC– Ti [1]  | Silicon wafer | Magnetron sputtering | Time = 180 min, Pressure = 0.3 Pa, Voltage = 75, 125, 175, 225 V, Speed = 5 rpm, Frequency = 40 kHz | Microwave generator, deposition chamber and pulse voltage supply | 1–2.4 |
| DLC [3]          | UHMWPE (D = 12 mm, t = 3 mm) | ECR–MPCVD | T = 60 min, Ar/C₂H₂ gas flow ratio = 0 : 1, 2 : 1, 5 : 1, Pressure = 0.5 Pa, Voltage = −200 V, Frequency = 15 kHz | PSII-IBED reactor | 0.04–0.08 |
| DLC [5]          | Ti (D = 9.51 mm, t = 0.63 mm) | Liquid-phase electrodeposition (N,N-dimethyl formamide, (DMF)) | T = 25°C | | |
| DLC [10]         | Ti–6Al–4 V (disc shape, D = 24 mm, t = 7.8 mm) | PSII-IBED | Time = 240 min, Voltage = 1200 V, Electodes distance = 4 mm, Time = 60–80 min | PSII-IBED reactor | 2–3 |
| DLCH [55]        | UHMWPE (Disc shape; D = 20 mm, t = 3 mm) | RF–PECVD | Voltage = 200 V | RF capacitive coupled reactor with plate parallel electrodes | 0.25–0.7 |
| DLCH [55]        | UHMWPE (Disc shape; D = 20 mm, t = 3 mm) | RF–PECVD | Voltage = 200 V | RF capacitive coupled reactor with plate parallel electrodes | 0.25–0.7 |
| DLC [4]          | Ti–6Al–4 V alloy (Disc shape; D = 25 mm, t = 4 mm) | RF–PECVD | Frequency = 13.56 MHz | RF plasma system | 2.5 |
| Coating Material | Substrate | Deposition method | Deposition parameter | Equipment | Thickness (µm) |
|------------------|-----------|-------------------|----------------------|-----------|---------------|
| Functionally gradient DLC—Ag, functionally gradient DLC—Ti [8] | Ti–6Al–4V | Pulsed laser deposition | Power = 0–2500 W Speed = 3 µm h⁻¹ Substrate T = 500 ºC Argon etching = 60 min Time = 40 min | Pulsed laser deposition chamber | 0.05 |
| DLC [11] | CoCrMo | Plasma source ion implantation | Time = 2 h | Plasma chamber with methane (CH₄) or acetylene (C₂H₂) gas flow | 0.2 |
| USND [17] | Ti–6Al–4 V (disc shape, D = 25.4 mm, t = 3.4 mm) | MPCVD | Chamber pressure = 65 Torr | Wavemat MPCVD reactor with He/H₂/CH₄/N₂ gas mixture | – |
| DLC [80] | Ti–6Al–4 V (D = 38 mm, t = 17 mm) | PACVD | Substrate T = 690–720 ºC Power = 0.93–1.1 kW Frequency = 13.56 MHz | RF chamber with acetylene (C₂H₂) | – |
| DLC [63] | Nanosized Ni dots on a Si | RF-PACVD | Pressure = 1.33 Pa Speed = 50 sccm Time = 2 h Voltage = −1000 V Voltage = −150 V | Methane as precursor gas | – |
| Cr/DLC [26] | Cold work tool steel AISI D2 and AISI 5210 (DIN 100Cr6) (Disc, D = 16–25 mm, t = 2–3 mm) | Anode layer source | Pressure = 1.3 × 10⁻⁹ mbar Substrate T = 70 ºC Current = 0.05–0.11 A Power = 50–330 W Time = 145–375 min Discharge voltage = 1–3 kV | ALS340L linear anode layer source from Veeco Instruments (Woodbury, USA) | 1.1–1.6 |
| Coating Material | Substrate | Deposition method | Deposition parameter | Equipment | Thickness (µm) |
|------------------|-----------|-------------------|----------------------|-----------|---------------|
| TiAlN/DLC [26]   | Stainless steel (D = 1 cm) | Magnetron sputtering | Ar flow rate = 130 sccm | Vacuum chamber with magnetron sputtering source | 1.5 |
|                  |           |                   | N₂ flow rate = 170 sccm |           |               |
|                  |           |                   | Power = 9.5 kW |           |               |
|                  |           |                   | Voltage = −80 V |           |               |
|                  |           |                   | Substrate T = 400 °C |           |               |
| TiN, titanium niobium nitride (TiNbN), titanium carbonitride (TiCN) [70] | Stainless steel | Arc evaporation PVD | Voltage = 100 | METAPLAS coating machine with nitrogen and acetylene gas flow |
|                  |           |                   | Current = 200 A |           | 0.002–0.005 |
|                  |           |                   | Gas pressure = 1.4 × 10⁻² mbar |           |               |
|                  |           |                   | Power = 350 W |           |               |
| TiN [9]          | Pure Ti   | Laser deposition   | Speed = 10 mm s⁻¹ | Laser Engineered Net Shaping (LENS™) system | 3000 |
|                  |           |                   | Powder feed rate = 15 g min⁻¹ |           |               |
| TiN [2]          | Stainless steel | Magnetron sputtering PVD | Substrate T = 300 °C | Magnetic sputtering system | 3 |
DLC coatings exhibit greater hardness than GLC, Ta and TiN in general. The hard coating provides protection in the presence of third body wear such as polymeric or cements debris. A lower wear rate can be achieved if the coatings have high hardness and low friction. As shown in figure 6, UNSD coating has the highest hardness value (65 GPa). DLC coated on Ti–6Al–4 V by plasma source ion implantation—ion beam enhanced deposition (PSII-IBED) has the highest surface roughness of 100 nm [10]. Huang et al [4] reported a much lower surface roughness (6.8 nm) for DLC coated on Ti–6Al–4 V using RF plasma enhanced CVD (RF-PECVD).

Hardness and elastic modulus of the DLC coatings have been known to vary over a wide range with $sp^3/sp^2$ bonding ratio, which depends on the kinetic energy of the carbon species and amount of hydrogen. The hydrogen is believed to play a vital role in the bonding configuration of carbon atoms by stabilizing tetrahedral co-ordination $sp^3$ bonding of the carbon species. The higher hardness and elastic modulus of the coatings implies that these coatings have a higher ratio of $sp^3/sp^2$ [52]. High residual stress is one of the main disadvantages in DLC coatings. This can cause poor surface adhesion and early delamination in the coatings. Interlayers such as titanium (Ti), CrC and silicon nitride ($Si_N$) can be used to improve the adhesion of the surface. An interlayer can be the physical barrier between the substrate and the corrosive environment in minimizing the risk of delamination. Doping DLC coatings with elements such as silver (Ag), nitrogen (N), fluorine (F) and titanium (Ti) is another method to further prove that silver particles in suspension can only be the physical barrier between the substrate and the corrosive environment in minimizing the risk of delamination. The performance of doped samples deteriorates due to the increase of bactericidal activity after a long period. Sondi et al [53] further proved that silver particles in suspension can only provide protection against early infection but cannot provide long lasting resistance against bacteria.

The structure of DLC films can be described as a dispersion of diamond nodules in a graphite matrix. It is inherently metastable and it will transform to graphite at high temperatures [54]. DLCH coatings showed a faceted structure of about 2–5 µm in size [55]. It was similar to the studies reported for very thin DLCH films (~50 nm) deposited on high density PE [56].

### 3.4. Tribological outcome of coating

Many attempts have been made to minimize the friction and wear of implant materials including the use of different sizes, shapes and clearances (design parameters) in artificial hip or knee implants. Hip simulator testing has shown that metal on metal bearing has a conferrable low linear (40 times) and volumetric (200 times) wear than a metal-on-UHMWPE couple [57]. However, a few studies have shown evidence...
### Table 3. Mechanical properties of selected coated surfaces.

| Sample                                | Hardness (GPa) | Elastic modulus, \( E \) (GPa) | Surface roughness, \( Ra \) (nm) | Structure and morphology                                    |
|---------------------------------------|----------------|-------------------------------|----------------------------------|---------------------------------------------------------------|
| Ta–CoCrMo applied load = 10 mN        | 23–37          | 254–316                       | 5–12                             | Homogeneous matrix with distributed carbides [6]             |
| Ta–Biodur (1000 °C, 60 min)           | –              | –                             | 40                               | Continuous without cracks or voids with single phase (CoTa)   |
| Ta–Co (800 °C, 60 min)                | –              | –                             | 136                              |                                                               |
| GLC–Si                                | 24.5           | –                             | –                                |                                                               |
| GLC–TiC–Ti–Si applied load = 100 nm   | 7.2–11.7       | –                             | 7.1–11.6                         | Amorphous with spherical particles of 10–20 nm particle size,  |
|                                       |                |                               |                                  | Columnar-free structure with film deposited at 225 V [1]     |
| DLC–UHMWPE                            | 0.139          | –                             | –                                |                                                               |
| Applied load = 10 mN [3]              |                |                               |                                  |                                                               |
| DLC–Ti                                | –              | –                             | 50                               | Film surface is regular and smooth. SEM image showed small    |
|                                       |                |                               |                                  | cracks in the film [5]                                       |
| DLC–Ti–6Al–4 V Applied load = 15 g    | 13.7           | –                             | 100                              |                                                               |
|                                        |                |                               |                                  |                                                               |
| DLCH–UHMWPE                           | –              | –                             | –                                | DLCH coatings showed a faceted structure of about 2–5 µm size |
|                                        |                |                               |                                  |                                                               |
| DLC–Ti–6Al–4 V Applied load = 0.5 mN  | 34             | 200                           | 6.8                              | Smooth, uniform, light brown surface Good adhesion to the    |
|                                        |                |                               |                                  | substrate [4]                                                |
| DLC–Ag                                | 32             | 288–299                       | –                                | Buckling shape [8]                                           |
| DLC–Ti                                | 27–29          | 253–274                       | 41.5                             |                                                               |
| DLC–CoCrMo [11]                        | 14.8           | –                             | –                                |                                                               |
| UNSD–Ti–6Al–4 V                       | 65 ± 5         | 400 ± 24                      | 4.3–14                           | Diamond structure with grain size between 4 and 6 mm [17]    |
| DLC–Ti–6Al–4 V [80]                   | –              | –                             | –                                |                                                               |
| Nano-undulated surface with DLC film  | –              | –                             | 0.6–13.7                         | Atomically smooth [63]                                       |
| Cr/DLC [26]                            | 14.7–30.4      | –                             | 3–14                             |                                                               |
| TiAlN/DLC [26]                         | 12.8 ± 3       | –                             | 30                               | Aggregates of about 80–150 nm in diameter [70]               |
| TiN                                   | 22–26          | –                             | –                                |                                                               |
| TiNbN                                 | > 30           | –                             | –                                | Free from any gross defects such as porosity and cracks [9]   |
| TiCN                                  | > 30           | –                             | –                                |                                                               |
| 40% TiN–Ti–6Al–4 V                    | 11.2           | –                             | –                                |                                                               |
| Applied load = 300 g TiN [2]           | –              | –                             | 169                              |                                                               |

of high toxicity due to generated metallic or UHMWPE particles [58–60]. Therefore, an appropriate coating does not only improve upon friction and wear but also increases the acceptability of implanted joints. Tribological tests concerning adherence, friction and wear properties in atmospheric and lubricated conditions are presented in table 4. Wear damage to the articulating surface is associated with the frictional forces at the interface. The coefficient of friction depends on the materials and the surface finish of the articulating surfaces in the lubricating regime. A better wettability will increase the lubrication, thereby decreasing the coefficient of friction and subsequently reducing the wear.

Ta coating with a lower surface roughness value gives a better wear rate. Ta coated on CoCrMo with a surface roughness of 5–12 nm exhibited a lower wear rate in the range of \(4 \times 10^{-7}–5 \times 10^{-7}\) mm\(^3\)N\(^{-1}\)m\(^{-1}\) [6] compared to Ta coated on the biodur alloy with 40 nm of surface roughness and wear rate in the range of \(0.755 \times 10^{-4}–1.249 \times 10^{-4}\) mm\(^3\)N\(^{-1}\)m\(^{-1}\) [7].

GLC coatings have high adhesion normally associated with a high ion current density magnetron sputter ion plating system. Low wear rates can be obtained when high hardness is combined with low friction. The excellent mechanical properties with good adhesion of the GLC coatings will result...
in high load-bearing capacity. GLC has a wear coefficient about ten times lower than conventional hydrogenated DLC coatings. GLC also has a lower coefficient of friction. Adhesion tests were used to reveal the quality of the coatings in terms of their abrasive wear potential in artificial joints. The surface scratch resistance of GLC coating prevents implant damage at excessive contact load up to 140 N. The scratch formation is minimal, which results in a substantial reduction in wear at $3 \times 10^{-8}$ mm$^3$ N$^{-1}$ m$^{-1}$ as opposed to DLC coatings [24].

Minn and Sinha [61] pointed out that intermediate layers like chromium nitride, TiN and DLC can be used to enhance the load carrying capacity and the wear resistant of the polymer film. The wear durability is higher with UHMWPE as the top layer is followed by an intermediate layer of hard DLC on Si substrate. UHMWPE was chosen because of its better wear resistance compared to other polymers such as polyetheretherketone, polymethyl methacrylate, polystyrene and polytetrafluoroethylene [62]. In addition, the top UHMWPE film reduces the shear stress and the coefficient of friction due to its self-lubricating property. The increase hardness of intermediate layers improves the wear performance.

Surface wettability is determined using water contact angle measurement. A low water contact angle gives a hydrophilic surface which can generally provide better adhesion. However, the hydrophilic surface has the tendency to attract more water molecules from the atmosphere if the humidity is high. The adhesion strength between the film and the substrate will decrease with the presence of water molecules on the solid substrate. Tribological tests showed that a higher hardness in the intermediate layers gives better penetration resistance to soft UHMWPE film, reduces the contact area of the ball and promotes wear durability.

Figure 6. Variation of hardness and surface roughness of the coated materials (zero values indicate the data are not mentioned in the papers selected).

We further investigated the variation of hardness and surface roughness of the coated materials. The results are shown in Figure 6. The hardness and surface roughness of the coated materials are plotted against the load. GLC has the highest hardness and lowest surface roughness compared to other coatings. GLC also has a lower coefficient of friction.

Surface roughness is an important parameter in tribological studies. A lower surface roughness results in lower wear rates. The GLC coating has a significantly lower surface roughness compared to other coatings.

Figure 7 shows scanning electron microscopy (SEM) images of DLCH coatings before and after wear testing. The comparison between the morphologies observed before and after testing confirmed the effectiveness of DLCH coatings in reducing wear. SEM observations of the wear tracks for 700 nm thick DLCH coated PE showed the presence of the same initial structure although it was grooved by long channels a few microns wide.

Figure 8 clearly demonstrates the variation of wear rate and contact pressure with different coating materials. Ta coating has a lower wear rate $\left(4 \times 10^{-7}$ mm$^3$ N$^{-1}$ m$^{-1}\right)$ with a

Wear and friction are greatly reduced by using DLC in total hip and knee replacement devices. The wear rate and the coefficient of friction of the coated surface are measured using a commercial ball-on-disc tribometer. Wear test is carried out in a rotating vessel with UHMWPE discs immersed in bovine serum (b-9433, Sigma Aldrich). Wear factors, $k$ can be calculated using the following equation:

$$k = 2\pi r A / Ls,$$

where $r$ is the wear track radius, $A$ is the average worn area, $L$ is the applied load and $s$ is the sliding distance [55].

The wear rate of the coating is very dependent on the variables like liquid lubrication, temperature and DLCH composition. The wear rate decreased with the sliding distance. An initial polishing of the sample and an associated increment of the contact area result in reduced contact pressure. Cross linked UHMWPE and pristine UHMWPE showed improved wear resistance compared to uncoated materials, which made them suitable for substrate with thin coatings. DLCH is an ideal option in modular implants as it provides better wear resistance and good adhesion to the substrates [55].
Table 4. Tribological performance of coating surfaces.

| Sample | Experimental parameters (pressure, speed, temperature, contact angle, lubrication, roughness and cycles) | Tribological performance matrix | Surface condition after tribological testing |
|--------|----------------------------------------------------------------------------------------------------------------|-------------------------------|-----------------------------------------------|
| Material: Ta-CoCrMo | Pressure = 9.9 GPa | Wear rate (mm³ N⁻¹ m⁻¹): 4 × 10⁻⁷–5 × 10⁻⁷ | Friction rate: 0.18–0.19 | First cracks (buckles and chevron type) appeared in the range of 7–9 N for wrought alloy and 11–16 N for casting Delamination began at 11 N [6] |
| Shape of specimen: ball on disc (alumina) | Force applied = 7 N | Speed of rotation = 10 cm s⁻¹ | Total disc rotations = 25 000 laps | Radius of wear track = 4–10 mm | Sliding distance = 628–1571 m | T = 37°C | Lubrication = dilute bovine serum |
| Material: Ta–Biodur | Pressure = 0.7 and 1.6 GPa | Wear rate (mm³ N⁻¹ m⁻¹): 1.249 × 10⁻⁴–0.755 × 10⁻⁴ | Friction rate: 0.22–0.75 | | Cracks observed at a load of 55 N. High scratch resistance, where Ta was still detected inside the Scratch at 100 N [7] |
| Shape of specimen: Pin on disc | Force applied = 5 and 7 N | Speed = 10 cm s⁻¹ | Total disc rotations = 25 000 | Radius of wear track = 3 mm | Sliding distance = 785 m | T = 37°C | Contact angle = 48° | Lubrication = dilute bovine serum |
| Material: Ta–Co | | | | | | | |
| Shape of specimen: pin on disc | Material: Ta–Biodur | – | 0.18–0.19 |
| Shape of specimen: ball on disc (alumina) | Material: Ta–Co | – | 0.18–0.19 |
| Shape of specimen: ball on disc (alumina) | Material: GLC–Si | Pressure = 3.5 GPa | Wear rate (mm³ N⁻¹ m⁻¹): 3 × 10⁻⁸ | Friction rate: 0.04 (water) | Failure in scratch adhesion test up to 140 N [24] |
| Shape of specimen: pin on disc (D = 14 mm) | Material: GLC–Si | Force applied = 10–80 N | Speed = 20 cm s⁻¹ | Total disc rotations = 318–477 rpm | Radius of wear track = 3 mm | Lubrication = dilute bovine serum |
| Material: GLC–Si | Shape of specimen: ball on disc (tungsten carbide, D = 5 mm) | – | 0.1–0.06 |
Table 4. (Continued.)

| Sample | Experimental parameters (pressure, speed, temperature, contact angle, lubrication, roughness and cycles) | Tribological performance matrix |
|--------|----------------------------------------------------------------------------------------------------------|---------------------------------|
|        |                                                                                                          | Wear rate (mm³ N⁻¹ m⁻¹) | Friction rate | Surface condition after tribological testing |
| Material: GLC–TiC–Ti–Si | Pressure = 2.3 GPa  
Force applied = 15 N  
Speed = 2 cm s⁻¹  
Total disc rotations = 20000 laps  
Radius of wear track = 1.5 mm  
Sliding distance = 189 m  
T = 37 °C  
Lubrication = paraffin | 10⁻⁹ | 0.045 | A small quantity of wear debris is observed on the surrounding of the worn scars [1] |
| Material: GLC–TiC–Ti–Si | Pressure = 0.35 GPa  
Force applied = 1 N  
Speed = 30 mm s⁻¹  
Total disc rotations = 10000  
Radius of wear track = 3 mm  
Sliding distance = 189 m  
T = 20 °C | 2.75 × 10⁻¹⁰ | 0.02–0.04 | No scratch found on the surface of UHMWPE with a C:H films coated when the stylus force increased to 10 mN [3] |
| Material: DLC–Ti | Pressure = 0.1 GPa  
Force applied = 2 N  
Speed = 2 mm s⁻¹  
Total disc rotations = 10000  
Radius of wear track = 2.5 mm  
Sliding distance = 157 m  
Volume = 3 × 10⁻³ m³  
Tracklength = 2 mm | 9.55 × 10⁻³ | 0.1 | -DLC film obtained from DMF ploughed off in specific sites without deformation of the substrate  
-A low amount of wear debris was observed [5] |
| Material: DLC–Ti–6Al–4 V–UHMWPE | Contact pressure = 0.01 GPa  
Force applied = 200 N  
Radius of wear track = 5 mm  
Sliding distance = 200–500 m  
T = 40 °C  
Lubrication = dilute bovine serum and 0.9% NaCl solution | 0.6 × 10⁻⁶–1.2 × 10⁻⁶ | 0.110–0.137 | High adhesion to Ti–6Al–4 V substrate of DLC gradient coatings  
Acoustic signal was observed at load 40 N  
Slight scratch observed after 2000 m sliding [10] |
| Material: DLCH–UHMWPE | Pressure = 0.037 GPa  
Force applied = 5.23 N  
Speed = 5 cm s⁻¹  
Radius of wear track = 4 mm | 2.4 × 10⁻⁶–3.0 × 10⁻⁶ | 0.11–0.20 | Presence of cracks and flakes, a mix of two phases appeared. The structure grooved by long channels a few microns wide  
Thickness of DLCH coatings remained onto PE substrates after 24 h of sliding [55] |
Table 4. (Continued.)

| Sample | Experimental parameters (pressure, speed, temperature, contact angle, lubrication, roughness and cycles) | Tribological performance matrix |
|--------|--------------------------------------------------------------------------------------------------------|----------------------------------|
|        |                                                                                                        | Wear rate                       |
|        |                                                                                                        | Friction rate                    |
|        |                                                                                                        | Surface condition after tribological testing |
| Sliding distance = 4400 m | Force applied = 1 N | – | 0.05–0.35 | Tiny scratch looked like fish bone with applied load of 200 mN at 400 mN, coating was ploughed, peeled off and delaminated [4] |
| $T = 37^\circ \text{C}$ | Lateral tangential displacement = 100 $\mu$m | | | |
| Lubrication = dilute bovine serum | | | | |
| Material: DLC–Ti–6Al–4 V | Pressure = 1 GPa | $10^{-7}$–$10^{-8}$ | 0.078–0.149 | Mild plastic deformation of the Ti–6Al–4 V substrate occurred at load 0.8 N. This indicated internal transverse cracking and external transverse cracking of the film [8] |
| Shape of specimen: ball on disc (corundum, $D=10$ mm) | Oscillation frequency = 10 Hz | | | |
| Force applied = 1 N | At 400 mN, coating was ploughed, peeled off and delaminated [4] | | | |
| $T = 23^\circ \text{C}$ | Lubrication = dilute bovine serum, Ringer’s USP solution | | | |
| Material: functionally gradient DLC–Ag, functionally gradient DLC–Ti | | | | |
| Shape of specimen: pin on disc | Force applied = 3 and 7 N | | | |
| Speed of rotation = 3 cm s$^{-1}$ | Total disc rotations = 300 000 laps | | | |
| Amplitude of wear track = 6 mm | | | | |
| $T = 37^\circ \text{C}$ | Lubrication = dilute bovine serum, Ringer’s USP solution | | | |
| Material: DLC–CoCrMo | Pressure = 1.03 GPa | $1.5 \times 10^{-5}$ | 0.2–0.3 | CoCrMo substrate was exposed by catastrophic cohesive failures [11] |
| Shape of specimen: pin on plate (Diameter of pin = 6 mm, length = 20 mm) | Force applied = 5.5 N | | | |
| Speed of rotation = 15 mm s$^{-1}$ | Total disc rotations = 5000 cycles | | | |
| Radius of wear track = 2.24 mm | Stroke length = 30 mm | | | |
| $T = 23^\circ \text{C}$ | Lubrication = fetal bovine serum | | | |
| Material: UNSD–Ti–6Al–4 V | Force applied = 15–130 N | $7.4 \times 10^{-7}$ | – | No wear was seen in the pin and disc combinations coated with multilayered USND coatings No coating delamination occurred after wear test [17] |
| Shape of specimen: pin on disc | Total disc rotations = 2 million cycles | | | |
| $T = 37^\circ \text{C}$ | Lubrication = bovine calf serum | | | |
| Material: DLC–Ti–6Al–4 V | Pressure = 0.0008 GPa | $7 \times 10^{-4}$ | 0.05 | Coating failure occurred after 4.1 km of wear [80] |
| Shape of specimen: pin on plate (alumina ball, $D = 5$ mm) | Force applied = 4 and 16 N | | | |
| Speed of rotation = 8 and 32 mm s$^{-1}$ | Sliding distance = 8 mm | | | |
| $T = 37^\circ \text{C}$ | Lubrication = phosphate buffer saline solution | | | |
| Sample | Experimental parameters (pressure, speed, temperature, contact angle, lubrication, roughness and cycles) | Tribological performance matrix |
|--------|-----------------------------------------------------------------------------------------------------------------|---------------------------------|
| Material: DLC–Si  | Pressure = 0.53 GPa, Force applied = 4 N, Speed of rotation = 17.3 cm s⁻¹, Total disc rotations = 4000–12 000 cycles, Sliding distance per cycle = 4.7 cm, T = 37 °C | Wear rate = 3.8 × 10⁻¹⁰–1.8 × 10⁻⁹ m⁴ N⁻¹ m⁻¹, Friction rate = 0.17, Surface condition after tribological testing = Wear scar appeared [63] |
| Material: Cr/DLC | Pressure = 0.0001 GPa, Force applied = 10 N, Speed of rotation = 5 cm s⁻¹, Total disc rotations = 150 000 laps, Sliding distance = 4.7 km, T = 24–27 °C | Wear rate = 1.2 × 10⁻⁸–2.5 × 10⁻⁷ m⁴ N⁻¹ m⁻¹, Friction rate = 0.05–0.15, Surface condition after tribological testing = Adhesive failure observed at critical load of 40–80 N [26] |
| Material: TiAlN/DLC | Pressure = 3.5 × 10⁻⁷–1 × 10⁻⁶ m⁴ N⁻¹ m⁻¹, Force applied = 67.5 N, Speed of rotation = 4.6 cm s⁻¹, Sliding distance = 1000 m, T = 37 °C, Lubrication = Hank’s balanced salt solution | Wear rate = 3.7 × 10⁻⁶–4.3 × 10⁻⁴ m⁴ N⁻¹ m⁻¹, Friction rate = 0.15–0.4, Surface condition after tribological testing = – |
| Material: TiN [70] | Pressure = 0.0009 GPa, Force applied = 67.5 N, Speed of rotation = 4.6 cm s⁻¹, Sliding distance = 1000 m, T = 37 °C, Lubrication = Hank’s balanced salt solution | Wear rate = 15 × 10⁻⁴ m⁴ N⁻¹ m⁻¹, Friction rate = 0.25–0.4, Surface condition after tribological testing = Shallow and smoother worn tracks were observed after 1000 m of sliding in SBF, FESEM showed isolated cracking and chipping of the TiN particles [9] |
| TiNbN | Pressure = 0.0014 GPa, Force applied = 63 N, Speed of rotation = 2100 mm min⁻¹, Sliding distance = 1000 m, T = 37 °C, Lubrication = simulated body fluid (SBF) | Wear rate = 6 × 10⁻⁴ m⁴ N⁻¹ m⁻¹, Friction rate = 0.115, Surface condition after tribological testing = Flakes and elongated debris were found [2] |
high contact pressure (9.9 GPa) compared to GLC, DLC and TiN coatings. Though the wear rate of DLC on UHMWPE reported by Xie et al [3] and DLC on Si reported by Park et al [63] are in the range of $10^{-10} \text{mm}^3\text{N}^{-1}\text{m}^{-1}$, the contact pressure applied is low in this case.

3.5. Biocompatibility of coating materials with surrounding tissue

The biocompatibility of coated surfaces can be judged by bacterial adhesion, wettability, cell growth rate on the surface and cell death rate by the wear generated debris. Hydrophobic surfaces (contact angle higher than 90°) are good for bearing materials used in an acetabular prosthesis component in joint replacement [64]. It was suggested by the researchers that films with low hydrogen content and hydrophobic properties increased the rate of bactericidal activity [65].

A coating with antibacterial properties is extremely important in reducing the risk of infection. Ta is a biocompatible metal that possesses a porous structure similar to spongious bone as the commercial trabecular Metal for various orthopaedic applications [6, 64]. It is suitable for cell adhesion, proliferation and differentiation [21, 22] and deposited Ta oxide and nitride could be applied in cardiac and vascular devices [66, 67].

Pure Ta has a lower bacterial adhesion compared to commercially available materials used in orthopaedic implants [68]. This is due to higher wettability of Ta surface in both distilled water and cell media with contact angle of 51° and 48°, respectively [64]. Furthermore, the study confirms that the Ta surface has better interaction between cell and material as Ta has higher surface energy. The low porosity of Ta surface has sharp interface between coating and the interface, resulting in high fatigue resistance, which is applicable to early biological fixation. However, we could not find any paper that studied the protein deposition rate and synovial fluid contact angle on Ta coated surfaces.

GLC coatings have shown no biocompatibility problem when tested for use in artificial hip joints. The GLC coated hip joints will have an estimation of at least 50 years compared to uncoated joints with the usage of about 10 years [24]. Generally, it can be used in knees and other joints.

DLC films have proven to be biocompatible. Kwok et al [66] reported that the contact angles of DLC and phosphorus-doped DLC films in water were 68.4° and 16.9°, respectively, indicating that the wettability of DLC film was enhanced by phosphorus doping. P-doped DLC coating reduced the interactions with plasma protein giving rise to small variations in the conformation of adsorbed plasma proteins and preferentially adsorbed albumin. Cells like macrophages, fibroblasts and other human tissues have already been grown successfully on DLCs [69]. The biological response of DLC wear debris has been tested by growing bone marrow cells in the presence of DLC film fragments. Hauert [65] suggested that DLC would make good implant coatings as there was no cellular damage recorded compared to the control samples. Double bonds in the carbon react with reactive oxygen and subsequently remove the superoxide radicals which are naturally generated when neutrophils and immune cells attack pathogens in the body. This effect could be beneficial in the implantation where...
an external infection would be likely to occur when the wound is new and open. This biological response will prevent or cure the infection by restricting any damage to the surrounding body from the immune system [69].

Serro et al [70] revealed that TiN coated films showed no cytotoxic effect and no changes in cell morphology or cell death when compared to fresh culture medium and PE control discs. Human foetal osteoblast cells were spread and attached on TiN reinforced composite samples indicating its biocompatible property of the surface. Rapid growth of cells on composite surfaces with countless cell–cell contacts render a superior surface for bone cell adhesion. Nevertheless, fewer cells were observed on pure Ti–6Al–4 V alloy. Thus, TiN-reinforced Ti4Al4 V alloy composites are non-toxic and have improved cell materials interactions compared with uncoated Ti–6Al–4 V [9].

4. Discussion

The most suitable coating material used for hip or knee joints must have bio-tolerance and ability to withstand high cyclic loading in the presence or absence of body fluids. The wear of surface and friction coefficient can be reduced by an appropriate coating technique which increases the surface hardness and enhances solid lubrication. However, the efficiency of coating surface depends not only on the types of material properties but also types of substrate, coating density, adhesion and uniformity of the surface.

DLC coating has the lowest wear rate ($10^{-5}$–$10^{-9}$ mm$^3$N$^{-1}$m$^{-1}$) compared to hard materials like alumina (0.004 mm$^3$ per million cycles) [41]. However, formation of pinholes in the DLC coated surface is one of the drawbacks in using the liquid-phase electro-deposition technique. A nobler open-circuit potential (thermodynamically stable), around 0.1 V, and lower anodic current density until 0.9 V was presented in the films deposited using the carbon source of acetonitrile [5]. A few studies have revealed the presence of small cracks in the film and uncovered substrate areas due to gas evolution during the deposition process [71–73]. Therefore, the deposition parameters and properties of the electrodeposited DLC films should be further investigated. The wear rate for DLC coated on titanium substrate is $9.55 \times 10^{-3}$ mm$^3$N$^{-1}$m$^{-1}$ with contact pressure of 0.1 GPa [5]. Deposition of DLC coating using the liquid-phase electrodeposition technique is not recommended due to its higher wear rate compared to DLC coated by other chemical and PVD methods.

Hardness of the surface coatings is the primary material property in defining wear resistance. There is also evidence that elastic modulus has an important influence on wear behaviour. In addition, elastic modulus plays an important role in stress shielding, which is a key issue in the stability of hip or knee implants. Elastic strain, the ratio of hardness ($H$) and elastic modulus ($E$), is a mechanical property that determines the limit of elastic behaviour in a contact surface and their failure mechanism [74,75]. For example, the elastic strain values were 0.07 for biomedical grade PE, 0.03 for Ti–6Al–4V and 0.04 for CoCrMo [17]. On the other hand, the elastic strain values were estimated to be in the range of 0.09–0.12 for Ta coated on CoCrMo [6], 0.17 for DLC coated on Ti–6Al–4 V [4], 0.10 for functionally gradient DLC coated on Ti–6Al–4 V [8] and 0.16 for USND coated on Ti–6Al–4 V [17]. This result implies that Ta and DLC coated surface have better wear properties compared to the uncoated.
A low wear rate with a high contact pressure indicates a better coating surface for joint replacements. Ta coated implants are found to be strong, compatible and durable. Ta has advantages over DLC, GLC and TiN coatings used in current generation of orthopaedic implants. Besides, Ta coating enables the mechanical properties of the underlying surface to be retained whilst optimizing the wear characteristics. It has the potential to be an effective implant solution.

In addition, the wear rate is influenced by the surface roughness of coating surfaces. A higher wear rate at $6 \times 10^{-4}$ mm$^3$ N$^{-1}$ m$^{-1}$ is obtained for TiN coating when the surface roughness reached 169 nm [2]. It has been revealed that a minimum wear occurs when an optimum surface roughness exists. Mckellop [67] stated that increasing the surface roughness of ceramic surface resulted in higher wear of prosthetic joint. The significance of metal surface roughness for controlling the wear of acetal gear against a hard counterface even in real life operating conditions is confirmed [76].

In this study, GLC coatings are an alternate material for application in artificial joints due to their low wear rate in the range of $10^{-9}$ to $10^{-8}$ mm$^3$ N$^{-1}$ m$^{-1}$ with contact pressure of 2.3 GPa [1] and 3.5 GPa [24], respectively. The greater the stress at the contact surfaces between the femoral and tibial components, the quicker the degradation of the surface happens. Lower wear rate obtained for GLC coatings at high contact pressure implies a longer durability of the joint prosthesis. However, the deposition technique for producing GLC coating is limited to magnetron sputtering. Other types of deposition techniques such as CVD or laser deposition should be further investigated in order to obtain a low wear characteristic coating surface.

As shown in figure 8, DLC coatings are hard and possess a lower wear rate in general compared to conventional TiN coatings. DLC are also much more scratch resistant than TiN coatings in joint implants. SEM images reveal isolated cracking and chipping of the TiN particles on Ti–6Al–4 V composite coatings with 40% TiN (figure 9) [9].

5. Conclusion and future implications

5.1. Conclusion

This paper has carried out a comprehensive analysis on four main types of coating materials used in joint prostheses. Coating deposition methods, mechanical, tribological and biological properties of the coating surfaces are discussed and compared. The study concludes the following:

1. The biocompatible characteristic of Ta coated implants with low wear rate and high contact pressure could be the suitable selection in joint prosthesis applications compared to DLC, GLC and TiN coatings.
2. Elastic strain, the ratio of hardness ($H$) and elastic modulus ($E$) is an important parameter in determining the wear performance of coating materials used in joint implants.
3. A high quality coating with strong adhesion and smooth surface (low surface roughness) guarantees the longevity of joint replacements in terms of contact stress, friction and wear. Coating thickness, deposition methods and parameters take into consideration getting a uniformity and scratch resistant surface.
5.2. Future implications

Coated surfaces of DLC, Ta, GLC have shown better mechanical properties including surface roughness, hardness and elastic strain. They have better tribological properties in terms of wear rate. However, most of the studies have very low cycle number, apart from UNSD coated on Ti-6Al-4 V [6]. Moreover, an artificial joint faces a dynamic loading depending on different human gait. The papers selected for this review concentrate on contact pressure in the range of 0.1–10 GPa under static load and bovine serum as a lubricant (except Balla et al [9]). However, bovine serum is very different from the simulated body fluid of osteoarthritic (OA) patients. Finally, the generated wear debris from these coated surfaces was not tested to characterize their biological response to the surrounding tissue. Therefore, coatings in joint prostheses should be investigated with a larger number of cycles, with simulated body fluid of OA patients under a range of dynamic load. A genotoxicity test should be conducted to determine the biological response of wear debris generated from coated substrate.

Acknowledgments

This work was supported by High Impact Research Grant UM.C/HIR/06/ENG/10 from the University of Malaya & Excellent young researcher (CZ.1.07/2.3.00/30.0039) from Brno University of Technology.

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