DLC Films in Biomedical Applications

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Abstract Diamond-like carbon (DLC) has outstanding tribological properties and is, additionally, tolerated well by the body. Due to this advantageous combination of properties, research and development efforts have been made toward the use of DLC coatings in biomedical applications. It has been demonstrated that DLC coatings do not trigger any adverse effects on attached cells and that DLC can be considered to be biocompatible by in vivo and also many in vitro experiments. DLC surfaces also have an excellent haemocompatibility and DLC-coated cardiovascular implants such as artificial heart valves, blood pumps, and stents are already commercially available. The different studies presented demonstrate that DLC has the ability to reduce wear, more or less independently of the lubricant used, in load-bearing implants when sliding against metals or against DLC. However, it seems that when DLC slides against ultra high molecular weight polyethylene (UHMWPE) in the presence of body fluids, the good tribological properties that DLC shows in air could not be obtained. The in vitro experiments of DLC sliding against UHMWPE apparently showed different results, due to variations in experimental setups (ball-on-disk, hip or knee simulator, surface roughness) and especially the different liquids used as lubricants. In some medical applications such as guidewires, urinary tract catheters, and orthodontic archwires, the in vitro and in vivo experiments on DLC-coated parts showed an improved tribological performance. When implanting a DLC-coated material, it has to be considered that the reaction layer at the DLC/substrate interface has to have a high chemical durability under in vivo conditions to guarantee lifetime adhesion.

Keywords diamond-like carbon, DLC, amorphous hydrogenated carbon, biomedical application, load-bearing implant, hip joint, knee joint, interface, UHMWPE, lubricant

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1 Introduction

Nowadays, due to overaging of the population as well as the increasing average weight of people, an increasing number of load-bearing joints have to be replaced by artificial implants, mainly hip joints and knee joints but also, to a lesser extent, other joints such as spinal disks. Additionally, diseases like arthritis can also require the replacement of joints.

Different materials for joints, with specific advantages and disadvantages, are implanted today. In prosthetic hip replacements the most commonly used implant materials are a steel femoral head articulating against an ultra high molecular weight polyethylene (UHMWPE) acetabular cup. The average wear rate of the polymer cup is in the range of 20–60 mm^3/year mainly in the form of micrometer-sized wear particles. The approximately 10^{10}–10^{11} polyethylene particles generated a year (or about 50,000/each single step) have been identified as the main factor limiting the lifetime of the implants. The large number of these particles, their size, as well as their ability to adsorb endotoxins [1] can induce inflammatory reactions causing bone resorption, which may lead to implant loosening (aseptic loosening). When a ceramic femoral head is used instead of a metallic one, according to clinical investigation, the wear rate of the UHMWPE cup can be further reduced, on average by 50% [2], which is still a large number of particles. Metal on metal hip joints have wear rates in the range of 1–5 mm^3/year, which amounts to around 10^9-µm-sized particles. Additionally, increased metal ion blood levels are observed, which can cause a delayed-type metal hypersensitivity. These metallic particles also may adsorb endotoxins supporting aseptic implant loosening. Additionally, we have to keep in mind that the number of allergies is increasing at a rate of about 10% each year. It is not known if, in the future, humans will also develop new allergies against implant metals or metallic particles. Ceramic on ceramic joints show very low wear in the range of 0.05 mm^3/year [2]; however, they may crack and release millions of hard particles which cannot all be removed surgically. The replacement joint can, therefore, only be a ceramic on ceramic type, since metals or UHMWPE would be worn out quickly by ceramic particles that migrate onto the articulating surfaces. An overview article of the different materials and surface treatments used in load-bearing surfaces in human joint replacements was published in 1999 by Dearnley [3]. A comparative study of the performance of metallic and ceramic femoral heads, and especially the importance of the surface finish, was published by Dowson [2].

To overcome the problem of particle generation in artificial implants, the use of a very low wear coating material which is additionally biocompatible is required. Since diamond-like carbon (DLC) coatings are known to be biocompatible and are also known to have extremely low wear rates in many applications, the biotribology of DLC coatings has been investigated in vitro. Several hundred DLC-coated artificial joints have already been implanted; however, these turned out to be rather problematic. Two main fields of biological applications of DLC have emerged. One application is the coating of implants that are in direct contact with blood.

Among these are heart valves, blood pumps, and stents. Another application is the use of DLC coatings to reduce wear in load-bearing joints. The different results published on experiments with DLC-coated femoral heads sliding against polyethylene cups revealed unexpected problems. However, joints where both sides are coated with DLC show promising results in laboratory tests. For an overview of DLC coatings in biological applications see Ref. [4].

In the following sections, the biocompatibility of DLC surfaces will be described and thereafter the biotribology of DLC and especially the crucial influence of lubricants will be addressed.

2 Biocompatible DLC and Alloyed DLC Surfaces

When a material is implanted into the body it has to be biocompatible. In vivo, the implant materials have to withstand the corrosive environment and not cause inflammatory or repulsive body reactions or any other undesirable effect. Additionally, the materials have to perform their desired function, such as low wear and fast bone ingrowths, over a long time.

Usually, the expected tissue reactions are first assessed by in vitro cell experiments. However, cell experiments cannot determine the in vivo biocompatibility of a certain material, but cell tests, if successful, can describe the principal biological in vitro response of a surface and are, therefore, an important step toward in vivo testing.

A number of research groups have investigated cell behavior by growing different cell types in vitro on DLC and studying the cell response. Macrophages, fibroblasts, human myeloblastic ML-1, human embryo kidney 293 cells, and other cell types have been grown on DLC under different conditions, and cell responses such as proliferation rate, viability, cell adhesion, differentiation, cell morphology, and cytoskeletal architecture have been monitored.

Fibroblast cells, for example, cultured on DLC- and N-containing DLC films, showed an excellent cytocompatibility (cell-compatibility) by means of proliferation rate and morphological behavior. In Fig. 1, a scanning electron microscope (SEM) image is shown of two mouse fibroblast cells (M3T3 cell line) immediately after mitosis, which illustrates the cell activity. Additionally, the cells keep intense contact with the underlying cell layer by their filopodiae and the cell surfaces show a high density of microvilli.

These in vitro experiments, as well as the in vivo reaction of DLC-coated CoCr cylinders implanted for 90 days in the lateral femoral cortex of sheep, showed that the DLC-coated surfaces are well tolerated by the body [5]. Mohanty et al. [6] confirmed the in vivo biocompatibility on DLC-coated Ti samples implanted in the skeletal muscle of rabbits for up to 1 year. An overview of the reaction of different cells on DLC can also be found in review articles [7,8].

When a material is implanted into the body, in a first step, depending on the chemical situation at the surface, proteins will adsorb onto the surface. These protein

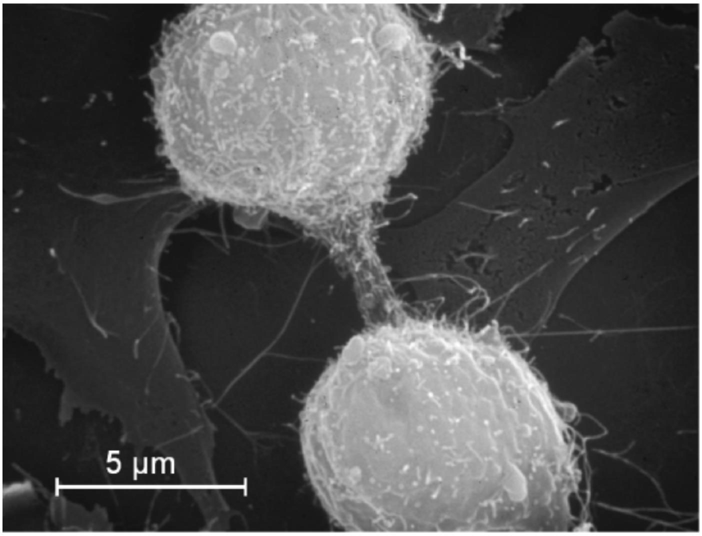

Fig. 1 SEM image of two mouse fibroblast cells after mitosis on a DLC substrate. The intense contact of the cells to the underlying cell layer by their filopodiae, as well as the high density of microvilli at the cell surfaces demonstrate the cell-compatibility of the DLC surface

distributions will then interact with the different cells and strongly influence cell attachment, cell proliferation, and cell differentiation. Additionally, on articulating surfaces of artificial joints, the wetting angle as well as the ability of a surface to attract biomolecules present in the synovial fluid (e.g., phospholipids, glycoproteins such as lubricin, albumin, hyaluronic acid) influence the biotribological behavior of the joint.

The surface chemical behavior of DLC can be easily tuned by the addition of different elements into the DLC film. This can be done by ion-beam implantation or by alloying DLC with other elements, which must also be biocompatible. By varying the alloy element concentration, it should be possible to tailor the biological reactions to any desired point between the properties of DLC and those of the added element. However, it has to be guaranteed that the alloyed DLC is also biocompatible. In the past years a few papers have presented experiments where the biological reactions on DLC have been changed by alloying. Especially the addition of SiO_x to DLC seems to result in a reduction of inflammatory reactions. Scheerder et al. [9] report on DLC-coated and DLN-coated or Dylyn (diamond-like nanocomposite, a Si:O containing DLC)-coated stainless-steel stents, which were implanted in pigs for 6 weeks. Their histopathological observation on the explanted stents showed that the inflammatory reactions, monitored by the number of inflammatory cells on the stent surface, were significantly higher on DLC than on DLN. Similarly, some companies (Sulzer CarboMedics and St. Jude Medical) use silicon-alloyed pyrolytic carbons (Pyrolite), a material that proved to be resistant to blood clotting, also indicating an improved biocompatibility by the addition of Si. Dorner-Reisel et al. [10] demonstrated that the addition of Ca-O to DLC decreased the film hardness, the wetting angle, and the fraction of sp^3/sp^2-bonded carbon. Cell tests with mouse fibroblast showed an increased number of cells, when compared to pure DLC, as well as improved cell viability for the Ca-O-DLC films. DLC samples containing different concentrations of titanium have also been examined in vitro to obtain a biocompatible surface that is hard, preventing abrasion and scratching. When Ti-DLC is exposed to a biological environment, the adsorption of different proteins could be altered as a function of the Ti content in the DLC film [11]. The adsorbed proteins will subsequently influence cell attachment, cell proliferation, and cell differentiation and probably even the tribological behavior. Bone marrow cell culture experiments on these Ti-DLC coatings demonstrated that the differentiation of bone marrow cells into bone resorbing cells, i.e. osteoclasts, is inhibited by the addition of Ti into the DLC [12].

When introducing a coating into the body, the long-term adhesion has to be guaranteed. Additionally, in the worst case of total film delamination, the generated particles should not have any harmful effects. It is known that materials that are tolerated well in bulk form are able to induce toxic reaction if present in particulate form, such as asbestos or quartz dust. Therefore, particles have been deliberately delaminated from a 500-nm-thick DLC film deposited on polyethylene foil as can be seen in Fig. 2 (left). From the average area of the particles of about $20\,\mu m^2$, a total film delamination in a hip joint would generate around 5×10^7 DLC particles. To investigate the biological reactions induced by delaminated DLC particles, bone marrow cell cultures have been incubated in vitro with these particles. The cells were able to internalize most of the particles within a few days, as displayed in Fig. 2 (right). Furthermore, the appearance of the cells was not different from the control cultures with no particles after 7 days. The addition of particles did not have any effect either on the cell viability or on the proliferation or differentiation, indicating that no toxic or inflammatory reaction of the body to

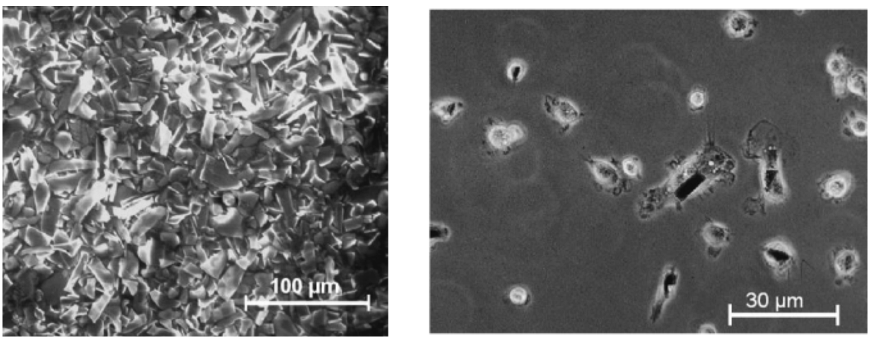

Fig. 2 (*Left*) SEM picture of deliberately delaminated particles from a 500-nm-thick DLC film. (*Right*) Phase contrast microscopy after 3 days in culture, bone marrow cells internalized the particles [13]

delaminated DLC particles may be expected [13]. Similarly, Aspenberg et al. showed that diamond or SiC particles, introduced into implanted bone harvest chambers in rabbits, did not cause any decrease in bone formation, whereas polyethylene, cobalt-chromium or bone cement particles caused inflammatory reaction and reduced bone ingrowth [14].

3 Blood-Contacting Applications

The excellent tribological properties of DLC are usually not of prime interest for blood-contacting applications; however, for some applications such as blood pumps and heart valves (friction in the hinges) the combination of the good haemocompatibility and excellent tribological behavior is required. For a more detailed description see Ref. [4] and other references therein.

For implants in direct contact with blood, a key issue is the ability of the implant surface to prevent thrombus formation. It is generally known that increased platelet adhesion, activation and aggregation on implant surfaces exposed to blood precede the formation of a thrombus. Therefore, in vitro analysis of these properties is usually performed as a first test of the haemocompatibility of a surface. Several papers of in vitro assays on DLC surfaces indicate that this material may have the ability to suppress thrombus formation similar to, or even better than, glassy carbon, a material widely used for heart valves. Maguire et al. describe the beneficial properties of Si-doped DLC for applications on stents and guidewires. By using Si doping, the mechanical barrier properties, and the in vitro response of DLC coatings have been improved [15]. Only a few papers present in vivo results of DLC-coated implants. In his Ph.D. thesis [16], Yang studied the haemocompatibility of different surfaces implanted for 2 h into the intrathoracic venae cavae of Swedish native sheep. The results showed that there were significantly more blood platelets on pyrolytic carbon and methylated titanium than on titanium, cobalt-chromium and DLC [16]. A DLC-coated centrifugal ventricular blood pump device (made by SunMedical Technology Research Corporation, Nagano, Japan) coated with DLC was implanted in calves and, even without postoperative anticoagulation, only minor evidence of thrombosis was found on the DLC-coated surfaces after explantation. Due to the good haemocompatibility of DLC, a few companies have DLC-coated implants already commercially available or in the state of development. The company Sorin Biomedica produces heart valves, annuloplasty rings, and stents that are coated by a so-called Carbofilm. A clinical study on the coated stents, implanted in 122 patients, showed a low restenosis rate of 11% after 6 months [17], whereas another medical follow-up did not show any difference in the restenosis rate between Carbofilm-coated and Carbofilm-uncoated stainless-steel stents [18]. Annuloplasty rings (used for heart valve repair) coated with Carbofilm have been implanted in sheep for 2–4 months and the explants showed an excellent biocompatibility and no thrombosis [19].

4 Tribology of DLC in Load-bearing Implants and the Influence of Lubricants

It is known that DLC shows a very low wear and also a low friction in atmosphere against most materials, except some polymers, and as shown in the last paragraph DLC can be expected to be biocompatible in in vivo applications. Furthermore, DLC has, when sliding in ambient atmosphere against certain materials, the ability to form a transfer layer on the softer counterpart, protecting it from wear. All this makes DLC a promising candidate for application on the articulating surfaces of orthopedic implants. For illustration, one of our own DLC-coated femoral heads is displayed in Fig. 3. A comparison of the potential of different coatings in hip replacement can be found in Ref. [20].

Many papers reporting on biotribological experiments involve either a ball-on-disk setup or a hip simulator to determine friction and wear of DLC-coated hip joint balls sliding against UHMWPE or of metal/metal joints with one or both sides coated with DLC. Depending on the test setup and especially the liquid lubricant used, different results can be found in the literature.

Fig. 3 DLC-coated femoral head of a hip joint

4.1 DLC-coated Femoral Heads Articulating Against UHMWPE Cups

As described in the introduction, in prosthetic implants consisting of a steel head sliding against UHMWPE, the polyethylene wear particles produced are the main cause for implant loosening. Making the steel surface harder with a DLC coating will probably protect it from scratches and corrosive attack (as with ceramic heads) but to lower the wear of the softer UHMWPE counterpart, the buildup of a transfer layer may be required. Additionally, it has to be considered that the adsorption of lubricating biomolecules on DLC may be different than on steel, which will also influence the tribological behavior. However, it is questionable if the buildup of a transfer layer on the polymeric cup can take place in a joint where body fluids are capable of reacting with wear products and of removing wear products out of the tribological contact area.

In the literature, experiments with different setups, especially different lubricants, are described. In cases where water or aqueous NaCl (aqNaCl) are used as lubricants, a reduction of the UHMWPE wear is usually obtained. Tetrahedral amorphous carbon (ta-C)-coated metal hip joint balls tested in 1 wt % aqNaCl with ball-on-disk and in a hip joint simulator showed a reduced wear of the UHMWPE cup by a factor of 10–100, compared to the uncoated samples [21,22]. A decrease of a factor of 5 in wear of the UHMWPE was obtained by coating the cobalt-chromium counterface with DLC when tested in a knee wear simulator using distilled water as a lubricant [23]. Different coatings have been tested with a ball-on-disk, also using distilled water as a lubricant, and a large decrease in UHMWPE wear was obtained with all the coatings. However, under these conditions, the thermally oxidized Ti6Al4V surface still performed about 8 times better than the DLC coating [24]. Analogously, DLC-coated stainless-steel femoral heads have been tested against UHMWPE cups in a hip joint simulator using distilled water as a lubricant. A decrease of the UHMWPE wear by a factor of 6 was obtained with the DLC coating. The same low wear rate of the UHMWPE was also obtained when using a zirconia femoral head under the same test conditions [25].

The setups described in this paragraph used diluted bovine serum. Saikko et al. [26] compared the wear of UHMWPE cups operated against CoCr, alumina, and DLC-coated CoCr hip joint balls in a biaxial hip wear simulator in the presence of diluted bovine serum. For all three combinations tested, they obtained wear rates of the UHMWPE cups between 48 and 57 mg/million cycles. Thus, they observed no significant difference in the wear due to the DLC coating and all wear values obtained are in the range known from clinical observations with CoCr and alumina hip joint balls. Similar results have also been obtained by Affatato et al. [27]. Femoral heads made from 316L stainless steel, alumina, CoCrMo, and DLC-coated TiAlV were tested in a hip joint simulator using bovine serum as a lubricant. They obtained wear rates of the UHMWPE cups between 25 and 37 mg/ million cycles for all four material used as femoral heads.

From the results shown above, it can be seen that, depending on setup and the lubricant used, different results on the wear of DLC sliding against UHMWPE are obtained. It was shown that, depending on the tribological conditions, DLC is able to form a transfer layer on the counterpart when using distilled water as a lubricant [28], which may explain the low wear results found when tested in water and aqNaCl. In the cases where bovine serum and synovial fluid are used as lubricant, the different biomolecules, especially phospholipids, glycoproteins, albumin, and hyaluronic acid adsorbed on the articulating surfaces, are able to strongly influence the tribological behavior in the joints. The transfer of polymer to the metallic surface and also the amount and size of particles produced are influenced by the biomolecular composition [29–33]. Analogous to Ref. [29], it was also shown that long polyethylene glycol chains attached in a brush-like arrangement on a surface are able to trap water in between their chains resulting in about 20-nm-thick fluid film (with increased viscosity of water) and a lower friction.

In joint simulators, it was shown that when the protein concentration is too low, the results may show a nonclinically relevant wear morphology [31] and variations in the serum protein concentrations produce different wear results [30]. Additionally, in a tribological setup, it has to be considered that a change of the conformational state of adsorbed biomolecules due to local overheating (thermal denaturation) can change the tribological outcome [31]. The surface texture also has a decisive influence on the wear behavior of a joint. Even single scratches, which may not be detected by an average surface roughness measurement, are capable of increasing the wear rate of UHMWPE by a factor of 30–70 [32].

In summary, it can be stated that wear tests on load-bearing implants having a polymer as a counterpart should be made with an adequate tribological setup such as an implant joint simulator. As a lubricant, a supply of a solution containing an adequate distribution of tribologically relevant biomolecules (such as serum or synovial liquid), has to be maintained to compensate for the proteins decomposed in the test due to high pressures between contact spots of the bearing [33]. From the different experiments shown above, it seems that no transfer layer is formed on the UHMWPE when sliding against DLC in biological media and the UHMWPE wear could not be lowered.

4.2 DLC-coated Femoral Heads Articulating Against Metal or Against DLC-coated Cups

Lappalainen et al. reported very low wear rates in metal/metal hip joints, with both sides coated with hydrogen-free DLC made by filtered pulsed plasma arc discharge (85% sp^3 bonding). The long-duration wear tests of 15,000,000 cycles (corresponding to about 15 years of implant use) with a hip joint simulator using bovine serum as a lubricant, which was replaced regularly to compensate for depleted proteins, showed extremely low wear below 10–4 mm^3/year [34]. Similarly, Tiainen investigated hip joints with both sides having an approximately 100-μm-thick layer of hydrogen-free DLC also made by filtered pulsed plasma arc discharge. Using a hip joint simulator and aqNaCl as a lubricant, a reduction of the wear rates, by a factor of about 10,000, corresponding to wear rates of 10^{-3} to 10^{-4} mm^3/year, have been reported [21]. Shi et al. tested steel, ceramic, and a 2-µm-thick DLC (a-C:H)-coated steel ball sliding against a flat steel plate and using bovine serum as lubricant. They found a large reduction of the ball wear by about a factor of 100, as well as reduced wear rate in the stainless-steel plate [35].

The clinically relevant tests made on a hip simulator in bovine serum did lead to very low wear rates; however, the tests performed in aqNaCl or with a pin on disk setup also led to comparable low wear values. It seems that in the case where DLC is articulating against DLC, the biotribological behavior does not change dramatically in the presence of proteins or that the buildup of a transfer layer may not be a key requirement for low wear (analogous to DLC/sapphire in atmosphere [36]).

4.3 DLC-coated Joint Replacements Articulating Against UHMWPE Implanted in Humans

To my knowledge, none of the global implant manufacturing companies sell DLC-coated load-bearing implants today. Dearnley [3] states in his review article, published in 1999, that he is unaware of any commercially available DLC-coated bearing surfaces for joint replacements. However, in recent years some materials and coating companies have offered DLC-coated implants. For example, the company Morgan Technical Ceramics offers in its news release (No. 4 July–December 2005) hip joints coated with Diamonex DLC. Until 2005, the French company M.I.L. SA (Matériels Implants du Limousin SA) commercially offered DLC-coated titanium shoulder joint balls and ankle joints with both parts (the tibial and the talar component) made from a nitrided AISI Z5 CNMD 21 steel and coated with DLC, but there is no published medical follow-up on the in vivo behavior of these implants.

In the two cases described below, DLC-coated knee and hip joints have been implanted, and in both cases a high rate of implant failure required revision surgery.

Up to 2001, the company Implant Design AG sold knee joints under the trade name Diamond Rota Gliding with the sliding area of the femur component coated with DLN (diamond-like nanocomposite, a SiO_x containing DLC described in reference [37]) that was sliding against a UHMWPE counterpart. Within a short time many of the ~190 implanted joints showed increased wear, partial coating delamination, as well as implant loosening. In July 2001, the implantation of this knee joint was forbidden by the Swiss Federal Office of Public Health (SFOPH).

A medical follow-up on 101 patients with DLC-coated femoral heads articulating against polyethylene was published in 2003 by Teager et al. [38]. The DLC-coated femoral heads with the trade name Adamante had been obtained from the company Biomecanique, France, and consisted of a 2–3-µm-thick DLC coating on a Ti6Al4V alloy ball, made by ion-beam deposition. While the DLC-coated implants showed no sign of problems within the first 1.5 years, thereafter more and more DLC implants showed aseptic loosening, requiring revision of the implant. The cause for aseptic loosening is the large amount of polyethylene wear particles, generated from the prosthesis, that initiate a macrophage-mediated inflammatory response, leading to osteoclast cells activation and resulting in bone resorption in the vicinity of the implant and finally implant loosening. Within 8.5 years, 45% of the implanted DLC-coated joints had to be replaced. The DLC coating on the retrieved joint heads showed numerous, mostly round, pits of complete film delamination whereas the remaining DLC film seemed to be undamaged.

In my opinion, the cause for the adhesive failure at the interface has to be attributed to the chemical stability of the DLC/Ti6Al4V interface. When a DLC coating is deposited onto a metallic substrate, usually about 1-nm-thick metal–carbide reaction layer is formed at the interface, which is responsible for good adhesion. Depending on the precleaning and the conditions at the very beginning of the DLC deposition process, the interface reaction layer may also consist of metal-oxy-carbide. On implantation, the long-term chemical stability of this interface reaction layer toward body fluids has to be guaranteed. That aqueous fluids, particularly phosphate buffered saline solution (PBS), can penetrate the coating through pinholes and slowly corrode the interface between DLC and a-Si:H/DLC is described in Ref. [39]. An example of oxygen containing instable interface, leading to ongoing interface corrosion and delamination, even during storage in ambient atmosphere, is given in Ref. [40]. In vivo interface corrosion involves the chemistry at the interface and probably also residual stress, the load pattern applied, and electrochemical aspects, and is not fully understood today.

5 The DLC Substrate Interface

As described above, the coating/substrate interface, in connection with the internal stress of the film and the applied load pattern during use, may be critical in determining the long-term coating adhesion. Therefore, an exact determination of the chemistry at the interface is required. Since the carbidic reaction layer at the interface usually has a thickness in the range of 1 nm, angle-resolved x-ray photoelectron spectroscopy (XPS) or XPS and Auger electron spectroscopy (AES) sputter depth profiling can be used to analyze the interface.

During depth profiling, the argon ion energies are usually between 500 and 5000 eV, which is more than the energy of chemical bonds and, therefore, depth profiling may alter the chemistry originally present at the interface [41]. On the other hand, the DLC films are deposited by ion-assisted processes, with the ions having energies between 20 and 200 eV, which is also higher than the energy of chemical bonds. Therefore, the interface chemistry observed during depth profiling of a DLC/metal interface displays the ability of the interface to form a reaction layer, but this is about the same interface chemistry as observed by nondestructive

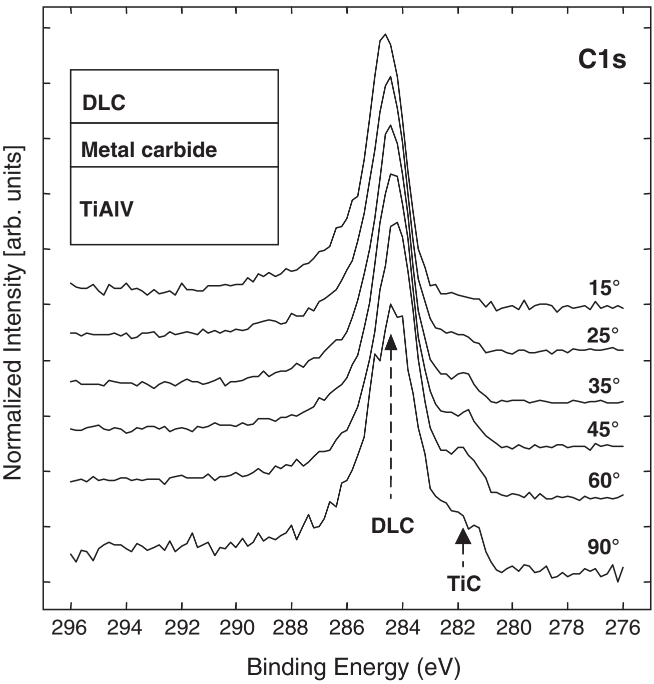

Fig. 4 Angle-resolved XPS analysis of a 5-nm DLC film on medical TiAlV. At high observation angle (perpendicular to the surface) the carbidic state of the interface can be seen

angle-resolved XPS. One main difference is that the carbidic interface reaction layer seen in depth profiles is usually thicker than the original interlayer determined by angle-resolved XPS [42]. Figure 4 displays an angle-resolved XPS analysis through a 5-nm-thick DLC film on TiAlV surgical alloy. The angles are given with respect to the surface. At high angles the carbidic nature of the interface can be observed by the appearance of the carbidic C1's contribution (mainly TiC) at 282-eV binding energy. From the analysis of the Ti, Al, and V electrons, we can determine that they are all in a carbidic state at the interface. Unfortunately, neither XPS nor AES can determine hydrogen, which, therefore, may or may not be present in the interface reaction layer.

The chemistry at an interface can be influenced or improved by the deposition of interlayers. In many industrial processes, ~50-nm-thick chromium, titanium interlayers or even multilayers are used. For implant materials, tantalum [43] and niobium interlayers are biocompatible and may show good interface properties. Additional, graded interfaces may also h ave some beneficial effects, since the grading allows an adaptation of the mechanical properties. On the other hand, the use of interlayers between the substrate and the DLC generates two interfaces, which both must adhere and be stable in the long term in vivo.

6 Other DLC Applications Connected to Tribology

There are other biomedical applications under development which may, depending on the success of research, be commercially available in some years. A few examples are given below. The torque used to insert or remove stainless-steel bone screws could be reduced by 50% with an amorphous diamond (AD) coating on the screws [44]. The DLC coating of medical guidewires could reduce the friction upon advancement by up to 33% and also particle generation and corrosion resistance could be improved [15]. Similarly, the DLC and F-DLC coatings on stainless-steel guidewires, tested in vitro under vascular conditions, resulted in a 30% reduction of the load, depending on the setup [45]. The University of Bonn reported that DLC-coated urinary tract catheters and ureter stents can prevent bacterial growth and incrustation. On the tribological side (inserting and replacing the catheter), the coated catheters are easier to insert and additionally the patients described the procedure with DLC-coated urinary tract catheters as substantially less unpleasant [46].

In dental correction, orthodontic archwires and brackets, usually made of stainless steel or NiTi, are used. The two main disadvantages of these alloys are the release of Ni ions, with the prevalence of allergic reactions, as well as a high coefficient of friction between the wire and the brackets. The archwire is designed to impose a force perpendicular to the wire (or along the radius of curvature) on the tooth, but a high coefficient of static friction will introduce unwanted tangential forces. It was shown by in vitro tests that the nickel ion release could be drastically reduced by a DLC coating [47,48]. Additionally, the coefficient of friction between the archwire and the brackets could be reduced, as shown by in vitro tests, with DLC-coated stainless steel and TiAlV archwires and brackets [49]. In humid air (75% R.H.) the static friction of steel against steel was measured to be 0.21 and it was reduced to 0.16 for DLC against steel [50] and to 0.15 for Si-DLC against steel [51]. On repeat experiments at the same positions the static coefficient of friction on steel against steel starts to scatter between 0.22 and 0.7 whereas it stays stable for the DLC and Si-DLC samples. For future successful applications, in vivo tests have to be performed on, for example, the adhesion of deposits by biomineralization and by bacteria, and its influence on the static friction.

7 Summary

In all the in vitro and in vivo cell culture experiments on DLC, no adverse effect of the coating on the cells has been observed and, therefore, DLC can be expected to be biocompatible in most in vivo applications. However, as DLC is a class of material, it has to be noticed that with altered deposition conditions, different biological reactions may be obtained. Therefore, any biological results on DLC should be correlated with an exact description of the deposition conditions, including pretreatment and a detailed characterization of the coating.

The different studies presented demonstrate that DLC has the ability to reduce wear, more or less independently of the lubricant used, in load-bearing implants when sliding against metals or against DLC. However, when DLC slides against UHMWPE in the presence of serum, the good tribological properties which DLC shows in air or vacuum cannot be obtained in load-bearing implants. The in vitro experiments of DLC sliding against UHMWPE showed different results, due to the different experimental setups (ball-on-disk, hip or knee simulator, surface roughness) and especially the different liquids used as lubricants.

In implant technology, issues like biocompatibility, long-term adhesion, corrosion stability, allergic reactions to corrosion products, and possible toxicity of delaminated particles have to be considered. In biotribology, additionally, the tribochemistry plays a crucial role and the adhesion of lubricating molecules to the surface, the reaction of wear products with lubricating molecules or biomolecules, the deposition of reaction products or biomolecules on the implant surface, as well as any cell reaction to wear products have to be considered. Furthermore, the applied load pattern, the amount of different lubricating molecules generated by the body, the cell reaction to wear products, etc. may also differ from patient to patient. Biotribology is a system property, involving the complex interaction of many factors and cannot be viewed as a sum of independent properties.

In some applications such as guidewires and orthodontic archwires, the in vitro experiments on DLC-coated parts showed an improved tribological performance. When implanting a DLC-coated material, it has to be considered that even the reaction layer at the DLC/substrate interface has to be chemically durable under in vivo conditions to guarantee lifetime adhesion.

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