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Biomedical applications of diamond-like carbon (DLC) coatings: A review

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Abstract

To resist wear, biomedical components require coatings that are exceptionally hard, have low friction, and are bioinert. Diamond-like carbon has been shown to provide this capability and to prevent leaching of metallic ions into the body. There are many ways to deposit such coatings from carbonaceous precursors, and some offer the means to incorporate other elements such as nitrogen, titanium, or silver. All reported tests of the biocompatibility of DLC coatings have been successful. This review will summarize work done on orthopedic and cardiovascular components together with other medical applications. For optimum tribological performance, the DLC must be deposited onto highly polished surfaces. The stage has been set for more simulation tests, leading to clinical trials, but the prospects appear to be very good.

Keywords: Diamond-like carbon; Biocompatibility; Leaching; Orthopedic components; Cardiovascular components; Importance of smoothness

1. Introduction

Coatings that are very hard, have low friction and are fully biocompatible have obvious applications in orthopedics, cardiovascular components, guidewires, etc. Diamond-like carbon (DLC) coatings provide these properties and have been the subject of much recent research which has revealed that care must be taken in order to achieve the best performance.

Though it is called "diamond-like", DLC is in fact not like crystalline diamond for it is black, not as hard, and is virtually amorphous. Its microstructure allows the incorporation of other species, and DLC comprises a family of such materials, the properties of which can be tailored far more readily than those of diamond. Hydrogen is frequently present in amounts up to 40 at.%, occupying regions of low electron density in the matrix. Its presence strongly influences the mechanical and tribological behavior of DLC coatings. Other additives often introduced include nitrogen, silicon, sulfur, tungsten, titanium, or silver.

As is well known, carbon–carbon interatomic bonds can be of two types: the near-planar trigonal or sp^2 form found in graphite, or the tetragonal sp^3 variety that occurs in diamond. It is the three-dimensional character of sp^3 bonding, together with the strength of the short C–C covalent bond that give diamond its great strength. DLC is intermediate in that it contains both types of bonding and clearly it is harder and more brittle if the sp^3 : sp^2 ratio is high.

Fig. 1 shows a cross-sectional TEM photograph of a typical DLC containing about 14% residual hydrogen, and it can be seen that there is no extended microstructure; the substance is nanocrystalline and this makes it relatively tough. It can also provide coating surfaces that are smooth on a nanometric scale.

There have been several attempts to produce useful biomedical coatings of crystalline diamond, but the disadvantage has been that these are rough and faceted due to the polycrystalline growth morphology. As a consequence, such surfaces produce excessive wear in the counterface material, and methods that might serve to polish them could

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Fig. 1. TEM micrograph of DLC coating showing graphitic nanostructure.

not easily be applied in a production situation, e.g., to femoral components.

2. Deposition of DLC coatings

Many methods have been developed for the deposition of DLC coatings, from a variety of carbonaceous precursor materials. They include:

- Direct ion beam deposition,
- Pulsed laser ablation,
- Filtered cathodic arc deposition,
- Ion beam conversion of condensed precursor,
- Magnetron sputtering,
- RF plasma-activated chemical vapor deposition,
- Plasma source ion implantation and deposition.

2.1. Direct ion beam deposition

The principle of this method is to bombard a surface, in vacuum, with energetic ions usually of methane so that, upon impact, the molecule dissociates and most of the hydrogen is liberated. Ion energies of 100 to 750 eV have been used, e.g., by Liu et al. [1] and the current density of about 2.5 A/cm^2 corresponds to an arrival rate of approximately 1.5×10^{16} carbon atoms/cm^2/s, most of which are retained. This is approximately a growth rate of 1 μm/h.

With a uniform atom-by-atom arrival, the coatings are very smooth and have Knoop microhardness of 6000 kg/mm^2 according to Liu et al. [1]. Though the residual hydrogen content is not stated, this hardness value suggests that it is relatively low. Against a zirconia pin the wear rates were below 10^{-7} mm^3/N m with friction coefficients for dry sliding of 0.02 to 0.10 increasing with relative humidity for reasons to be discussed below.

2.2. Pulsed laser ablation

Voevodin et al. describe a process for the deposition of DLC coatings using KrF excimer laser to vaporize material, in vacuum, from either a graphite target or one consisting of polycarbonate [2]. The latter results in hydrogenated DLC films sometimes designated as α-C:H. Steel substrates were either negatively biased as unbiased with regard to the target. Those coatings deposited under bias, from −100 to −800 V, have somewhat lower friction coefficients. The wear rates of the carbon films against sapphire pins were remarkably low at about 10^{-9} mm^3/N m while for the softer α-C:H films the wear rate was around 10^{-6} mm^3/N m at a contact pressure of 0.8 GPa.

A potential drawback to pulsed laser ablation (PLD) is that occasionally droplets or chunks of the target material are ablated and cause a surface roughness that is not easily removed. The internal stress can also be very high, but Wei et al. [3] have described a functionally graded DLC coating with reduced compressive stress and improved adhesion.

2.3. Ion beam conversion coatings

One of the more versatile methods for depositing DLCs is by the simultaneous ion bombardment and condensation of a low vapor pressure compound. The rupture of C–H bonds releases hydrogen into the vacuum leaving a largely carbonaceous coating. Deposition rates are high, up to 10 μm/h, and the compressive stress in such coatings is low (1 GPa or less), perhaps due to the progressive removal of hydrogen from within. The precursor materials may either be diffusion pump fluids or solids such as adamantane or coronene. Previous internal work at SwRI has shown that if ferrocene is used, the coating may contain up to 24 wt.% of iron. Siloxane precursors such as pentaphenyl trimethyl siloxane produce films with a few percent of silicon and oxygen, with advantageous properties, such as reduced dependence of friction coefficient or relative humidity. The ion energies used may range from 100 eV to 100 keV. Accounts of the process have been published by Fountzoulas et al. [4].

It is also possible to incorporate elements such as sulfur, fluorine, or nitrogen by choice of the precursor, and some of these assist in providing a low friction coefficient. The coatings produced by these methods are smooth, but due to the residual hydrogen content, typically 15 at.%, they are not as hard as amorphous carbon coatings, though they can still be comparable with hard tool coatings such as titanium nitride or alumina.

2.4. Filtered cathodic arc deposition

This is a method for producing very hard, virtually hydrogen-free DLC coatings. An arc is drawn in vacuum between a graphite cathode and an anode, typically at 50–60 A [5]. A radial magnetic field steers and filters carbon ions and rejects macroparticles. A bias voltage of 100 to 300 V is applied to the substrate.

That the filtering is effective is shown by the high degree of smoothness of the films. Xu et al. [5] report an R_a value of about 0.4 nm. Stresses in the coatings are high at -7 to -10 GPa and this contributes to coating hardness, that may reach superhard values of 40 to 50 GPa.

Such hardness is advantageous in resisting abrasive wear, but the high compressive stress means that there will be a tendency to decohesion unless adhesion is strong. Most of the reports refer to substrates of silicon or quartz, to which carbon adheres strongly.

2.5. Plasma source ion implantation and deposition

In this method, described by Anders et al. [6] a plasma is created in the work chamber and the workpieces are immersed in it. Periodic pulsing to around 2 kV accelerates carbon ions from the expanding plasma sheath during the pulse, of duration 1 ms. The carbon plasma may be formed by a pulsed cathodic arc, with a magnetic filter (as described above) to remove macroparticulates. The films are virtually free of hydrogen and are hard. Cui et al. report values up to 45 GPa, with low friction coefficients [9].

The compressive stress in such coatings is high, but Anders et al. describe a method for varying the substrate bias during deposition to produce alternating hard and softer layers with a net reduction in stress. Some of these coatings have been the subject of orthopedic testing (see below), with outstanding results.

2.6. Magnetron sputter coating

Magnetron sputtering is a widely used process for physical vapor deposition and it can be employed for carbon, though deposition rates are relatively low due to the low sputtering coefficient. Peng et al. [7] used DC magnetron sputtering as one of the four methods of deposition in the study of the smoothness of DLC coatings. Non-hydrogenated films up to 1 μm thick were prepared by sputtering from a pure graphite target in an argon plasma. A bias voltage was applied to the substrate and could be varied from 200 to 300 V. The argon pressure was around 1 Pa. Magnetron sputtering of carbon or forms of carbon nitride (CN_x) is used extensively to provide thin (3 nm) protective coatings on magnetic storage media, the nitrogen being introduced by reactive sputtering in an N_2/Ar plasma. Broitman et al. [8] described the application of such coatings to certain orthopedic substrates such as zirconia in order to reduce the friction coefficient against UHMWPE.

Because of the low sputtering coefficient of carbon this is not an efficient means for depositing thick (2–3 μm) coatings and possibly this is why it has not been investigated more widely in the biomedical field. An up-to-date review by Cui et al. [9] is shortly to appear with comparisons between DLC and carbon nitride coatings in terms of their orthopedic hemocompatibilities.

The technique of unbalanced magnetron sputtering for the deposition of amorphous carbon films has been described recently by Ahmad et al. [10].

2.7. RF plasma-activated chemical vapor deposition

Chemical vapor deposition, involving the thermal dissociation of a selected precursor is extensively used for coating tools and semiconductor devices. The addition of an electrical plasma lowers process temperatures. It is easy to apply the method for DLC, and Erdemir et al. [11] describe a careful study of the results of using four different source gases; namely, methane, ethane, acetylene and ethylene, at pressures of 1.3 to 1.7 Pa. The substrate bias was 1600 V, and the substrates were of steel. The lowest friction and wear, against steel balls, were obtained for methane, and the highest for acetylene. The authors attribute the difference to the hydrogen : carbon ratio, the role of hydrogen being possibly to promote a higher sp^3 content, or else to decorate the coating surface and reduce friction. Methane/hydrogen mixtures in the plasma (1 : 1) gave even lower friction, the coefficient against steel falling to 0.01. It is a pity that these results were not correlated with determinations of the residual hydrogen present in the coatings which can be done by elastic-recoil ion beam technique.

The wear resistance corresponded to the friction behavior being about 9×10^{-9} mm^3/N m for methane-grown films and two orders of magnitude greater for the acetylene-grown film. In conclusion, methane/hydrogen mixtures are shown to be best for tribological applications of DLC, and this work shows clearly that the method of preparation of the coating is very important.

3. The tribological properties of DLC

In many biomedical applications the wear rate and friction must be very low and the hardness of the coating must not induce excessive wear of the counterface material. It has been shown both experimentally and in computer (molecular dynamics) modeling that during sliding wear the outer layers of DLC are transformed to graphite oriented with its basal plane parallel to the surface. Subsequently, easy shear can occur at load-bearing asperities and as Liu and Meletis have reported [12] both friction and wear rates are very low.

The surface of carbon, whether bonded as diamond or graphite, is generally decorated by a monomolecular layer of hydrogen. For contact pressures up to about 1 GPa this film remains in place and greatly reduces the tendency for adhesion to the counterface, especially if it consists of a polymer such as polyethylene, the surface of which is also terminated by hydrogen atoms.

High humidity causes an increase in friction for reasons not well understood. Water molecules may bond to the hydrogen and simply provide a more reactive surface. Additions of a few percent of silicon to DLC substantially reduce this effect.

The surface roughness of hard coatings has a strong influence on the wear of the counterface, especially when this is a soft material such as UHMWPE. A careful study has been made by Peng et al. [7] of the roughness of DLC coatings prepared by three different techniques, and the effects of post-deposition treatments.

The methods chosen were RF plasma-activated CVD in methane, DC magnetron sputtering in argon, and a carbon ion beam extracted from a cathodic arc discharge. In each case the bias voltage applied to the substrate could be varied up to about 350 V. After deposition, some specimens were subjected to argon plasma sputtering, or to hydrogen etching in a plasma, or heat treatment at 500 °C in vacuum. The substrates were of silicon, argon sputter cleaned and had a roughness of only 0.046 nm.

The coating roughness was similar for all three deposition methods, but depended markedly on the bias voltage, as ion impingement energy, with the lowest values of about 0.04 nm being obtained at a bias of 250–300 V. Heating at 500 °C increased roughness, as did argon sputtering and hydrogen etching, which perhaps removes graphitic clusters from certain regions of the surface.

Thus, under preferred conditions DLC coatings up to 700 nm in thickness could be as smooth as a carefully prepared silicon crystal substrate, and we shall see below that in orthopedic applications this is highly beneficial.

4. Orthopedic applications of DLC

The load-bearing surfaces of total hip and knee arthroplasties are subject to wear and it is well recognized that the most serious consequences are those due to the formation of polyethylene debris at a rate of perhaps 10^{10} particulates per year. These particulates are phagocytosed resulting in granulomatosis lesions, osteolysis and bone resorption, causing pain and aseptic loosening of the prosthesis.

DLC coatings have been explored over the past ten years as a means for eliminating this problem, with some highly encouraging results. The goal is to demonstrate lower PE wear than what occurs against metals and ceramics such as alumina or zirconia. Fractures have occurred in ceramic femoral heads, and so a hard, low friction coating on metal would potentially be the best solution.

Some early investigations of DLC, by Davidson and Mishra, were beset by problems of high compressive stress and decohesion, but work referred to above has done much to reduce the likelihood of coating delamination, either by bond coats or control of coating stress.

Results over the past five years have indicated the excellent potential for DLC in total joint replacements, but the findings, though all good, have been variable and it is interesting to arrive at an explanation for this in terms of coating roughness and test procedure.

Saikko et al. [13] compared femoral heads of CoCr, alumina, and CoCr coated with DLC prepared by an RP plasma discharge in acetylene. Tests were done in bovine serum, with no additives, in an anatomical hip wear simulator operating at 1 Hz. The wear of UHMWPE over 3 million cycles was similar for each type of head.

Sheeja et al. [14] tested Co–Cr alloy disks coated with DLC by the filtered cathodic arc method and compared them with uncoated Co–Cr against UHMWPE pins in a simulated body fluid. The wear rates were similar, but it was found that the corrosion rate for the coated alloy was reduced by a factor of about 10,000. In subsequent work Sheeja et al. [15] explored the benefits of treating both the Co–Cr alloy and the UHMWPE with DLC and found a significant reduction in the wear rates of both sliding surfaces. If the polymer alone is coated, its wear rate is reduced but there was found to be severe wear of the Co–Cr. Prior implantation of these materials with C^+ ions before coating did not provide any superior behavior.

In an NSF-funded study, Xu and Pruitt [16] examined DLC coatings on Ti–6Al–4V alloy against UHMWPE in pin-on-disk tests in water. The DLC was prepared by the plasma source method described above. The rate of PE wear was reduced by a factor of 3–4, compared with uncoated alloy.

Onate et al. [17] used a knee wear simulation machine to compare Co–Cr, alumina, and Co–Cr coated with DLC from acetylene. In this case there was a substantial improvement over the uncoated alloy, by a factor of 4, and 40% less wear than against alumina.

A hip joint simulator was used by Lappalainen et al. [18] to compare DLC coatings on stainless steel, Ti–6Al–4V and CoCrMo alloy, by the filtered cathodic arc method, with a chromium bond coat. With ultra-smooth coatings with a roughness of 7 nm the wear rate of UHMWPE was reduced by factors of 30 to 600 times compared with the uncoated metal. Corrosion rates in 10% HCl were decreased by over 10,000 times. In a very recent invited review Lappalainen [19] mentions that amorphous diamond coating "can improve corrosion and wear resistance even by a factor of million compared to conventional materials" and he discussed "special procedures" to achieve these goals.

Affatato et al. [20] made use of a hip joint simulator to compare DLC coated titanium alloy with CoCr and alumina over 5 million cycles in bovine serum with addition of EDTA (ethylene diamine tetra acetic acid) to minimize precipitation of calcium phosphate, which they state can strongly affect friction and wear properties. The DLC, made by PACVD from methane, was comparable to alumina in terms of PE wear.

A comparison of these results shows that care must be taken with regard to the source of DLC, methane being superior to acetylene, and above all to the smoothness of the substrate. In hip joint simulator tests it is advisable to provide an additive to serum to inhibit calcification.

When conditions are favorable, the tests indicate that DLC coatings have the potential to provide the lowest wear rates of UHMWPE, perhaps half that against alumina, without the risks associated with fracture of ceramic components. Corrosion and leaching of metal into body fluids has been shown to be very markedly reduced by DLC coatings.

5. Biocompatibility of DLC coatings

It would hardly be possible to use DLC as a coating for items in vivo unless it has been shown to be biocompatible, and all studies to date agree this is the case.

In an early study, Thomson et al. [21] used mouse peritoneal macrophages and mouse fibroblasts on DLC prepared by the dual beam ion method, monitoring levels of lactate dehydrogenase (LDH) as a measure of cell viability. There was no indication of cytotoxicity. Similar results were obtained by Allen et al. [22] using the murine macrophage cell line, IC-21, in a growth medium supplemented with calf serum, or DLC made by plasma-activated CVD. Cell growth studies were made using human synovial fibroblasts and a human "osteoblast-like" cell line, SaOS-2. Cell growth kinetics were determined by counting after each 24 h incubation period, following disaggregation and staining. Cells grew well on DLC-coated glass and polystyrene with no evidence of abnormal morphology. Cells generally grew faster on DLC, adhered well, and produced extensive filopodia.

Butter and Lettington [23] report preliminary in vivo studies involving the implantation of DLC-coated pins into soft tissue and femurs of sheep. Much better bonding was observed at DLC rather than metal–tissue interfaces indicating a lower risk of infection. They also describe work done by Mitura on the coating of orthopedic screws with DLC by the RF plasma method. Over 52 weeks implantation of DLC-coated metal showed no evidence of corrosion products or chronic inflammatory reaction.

Ex vivo experiments with whole blood have shown that DLC-coated stainless steel and titanium compare well with LTI carbon and are superior to glass. There is a need, however, for in vivo trials, justified by the fact that all biocompatibility tests of DLC-coated surfaces have been successful, with no contrary indications.

In an extension of the biocompatibility of DLC, Steffen et al. [24] used it as a substrate for heparin following treatment in an ammonia plasma to form reaction amino sites for attachment. The optimum plasma exposure time at a pressure of 0.3 Pa was around 45 s. This treatment with heparin increased blood coagulation times from 25 to over 250 s.

Successful in vivo tests of the biocompatibility of DLC have been reported by Allen et al. [25] who implanted DLC-coated CoCr cylinders into intramuscular locations in rats and transcortical sites in sheep. After 3 months, histologic analysis showed that the specimens were well tolerated. Based on this excellent biocompatibility the authors have initiated a long-term animal study of a DLC-coated knee arthroplasty.

The most recent published work on biocompatibility has been that of Singh et al. [26] who evaluated DLC coatings for improved biocompatibility in chronic neurasthenic implants. They assessed the cytotoxicity and cell adhesion of DLC exposed to glial and fibroblast cell lines in vitro. DLC coatings did not adversely affect 3T3 fibroblast and T98-G glial cell function in vitro. There was also success in rendering DLC coatings non-adhesive by the application, by conventional means, of surface immobilized dextran.

Finally, for some applications, it can be reported from our own research that DLC adheres very strongly to silicone elastomers, probably due to the formation of strong Si–C bonds at the interface.

6. Cardiovascular applications of DLC

Heart valves are conventionally made from LTI carbon and, despite great care in manufacture, there remains a very small but finite risk of failure due to fracture initiated at an undetected surface or subsurface flaw. Therefore, there has been interest in replacing this brittle material with a metal coated with hard carbon that is non-thrombogenic.

Butter and Lettington [23] suggest the use of NiCr18 stainless steel coated by a non-line-of-sight method with carbon. The plasma conversion method would be a suitable choice. It has been reported that a silicon-containing DLC may be a better coating for cardiovascular purposes, but Butter and Lettington comment that in tests it showed no difference from the controls. The published studies all show DLC to be a promising biomaterial for heart valve applications and it is known that proprietary work is in progress on this topic.

Arterial stents can induce platelet activation and may initiate thrombosis by shear forces on the flow and by platelet adhesion to the metal. Gutensohn et al. [27] evaluated in vitro the performance of stents coated with DLC. Growth arrays using smooth muscle cells and endothelial cells showed that DLC did not affect proliferation rates and no cytotoxic effects were observed. Flow cytometric analyses showed no significant changes in mean channel fluorescence intensity for the structural antigens CD41a and CD42b, while by contrast expression of the activation-dependent antigens CD62p and CD63 increased significantly in uncoated compared with DLC-coated stents.

Release of metal ions into the bloodstream is a matter of concern, and Gutensohn et al. [27] used atomic adsorption spectrometry to detect a significant release of nickel and chromium ions into human plasma over a 96-h period, from non-coated stents. However, only minimal concentrations of released ions could be detected in the case of DLC-coated stents. Similar results were obtained by inductively coupled plasma mass spectrometry analysis, and in this case the release of metal ions from DLC-coated stents was “virtually undetectable.” The authors conclude that the coating of intracoronary stents with DLC may contribute to a reduction in thrombogeneticity and consecutively in the incidence of acute occlusion and restenosis in vivo.

Catheters have been coated at Southwest Research Institute with a mixture of silver and DLC. In vitro tests confirmed the efficacy of this coating for local freedom from bacterial infection. Diamond-like carbon coatings on segmented polyurethane were tested for blood compatibility by Alanazi et al. [28] and it was shown that they could be superior to an excellent non-thrombogenic polymer, 2-hydroxyethyl methacrylate (HEMA), in tests carried out in an parallel flow chamber. The authors conclude that greater attention should be paid to DLC for use in the medical field.

7. Other biomedical applications of DLC

Elinson et al. [29] applied thin coatings of DLC (20–200 nm) to soft contact lenses and contact lens cases to reduce the problems of biofilm formation. The authors regard microbial contamination of contact lenses to be as major a problem as that of the lenses themselves, and showed that lenses stored in DLC-coated cases were free from any contaminations.

McLaughlin et al. [30] investigated RF plasma deposited DLC on stainless steel medical guidewires and found good adherence with a coefficient of friction superior to that of PTFE. Furthermore, the thin DLC coating did not alter the overall stiffness of the guidewires, in contrast to PTFE or silicon coatings that may be up to 300 μm thick.

In ophthalmic surgery, the surgeon may need to suture the corneal region while causing the least distortion of the eyeball. Butter and Lettington [23] refer to experiments that have shown that a DLC coating on the needle reduces the force required to penetrate the cornea of pigs’ eyes by about 30%. There may be more such applications in microsurgery, and the authors point out that the dark color of DLC would have the further benefit of reducing reflections from the lights of operation microscopes.

8. Conclusion

While diamond coatings may have some applications in biomedicine, it is diamond-like carbon (DLC) that has emerged over the past decade as a most versatile and useful biomaterial. Harder than most ceramics, bioinert, and with a low friction coefficient, DLC is one of the best materials for orthopedic applications. If deposited with the preferred composition on a very smooth substrate, it offers the lowest wear rate of a UHMWPE counterface, below that observed against polished alumina or zirconia and without risks associated with fracture of a brittle ceramic.

All studies of the biocompatibility of DLC are in agreement that there is no cytotoxicity and cell growth is normal on a DLC-coated surface. Its blood compatibility is as good as that of the well-established LTI carbon used in heart valves. DLC coatings on stainless steel have performed very well in in vitro studies of haemocompatibility.

Undoubtedly there is more work in progress than has been reported in the open literature, and the stage has been reached at which in vivo testing of DLC is warranted. With cautious optimism, we look forward to the application of well-bonded DLC coatings in a variety of orthopedic and cardiovascular applications. All of these procedures, of total joint replacements, heart valves and stenting, for which DLC may provide greater efficacy and an extended service life, are ones which give patients a much greater quality of life.

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