

Medical Application of Diamond-Like Carbon (DLC) Coating-A Review

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1. Abstract

An artificial heart is a specific intervention that can be used to treat various heart diseases. Silicon oil is used as a pillar for the artificial heart. However, certain problems may arise as silicon oil ions diffuse with the blood through ion penetration. To solve this issue, it is recommended to use a coat pillar that is made from material that is highly biocompatible, exhibits low rates of penetration, and is stable, reliable, and durable. Many materials can be used for coat pillars, with research suggesting that the ideal coating material is diamond-like carbon. This coating is recommended because of its attractive physical, chemical, mechanical, and biocompatibility properties. DLC is a component of amorphous carbon material that contains some of the same properties of diamond. Moreover, because of its properties and benefits, we find that it can be used to coat many other materials.

2. Introduction

DLC was first introduced in 1971, having emerged accidentally during a research experiment on diamond that was subjected to vapor-phase synthesis. The 1950s can be highlighted as the phase when laboratory experiments for the synthesis of crystalline diamond at high pressure were in full swing. However, the process required specific equipment and proved to be costly. Subsequently, an increasing number of researchers aimed to prepare diamond crystals from vapor-phase synthesis using hydrocarbon gas and carbon vapors. These efforts led Aisenberg et al to publish an evidence-based study based on the development of a hard film (amorphous) that was made from carbon and given the name 'DLC' [1].

DLC exhibited several features that were superior to other interventions, such as a low friction coefficient, improved chemical stability, and firmness [2]. Therefore, the development of DLC films proved to be a valuable achievement in the realm of medicine.

There are seven forms of DLC, all of which have a high value of sp^3 hybridized carbon atoms. The different forms of DLC exist because the diamond is produced in two different crystalline poly-types. In the most general structure, the carbon atoms are arranged and regulated in a cubic lattice structure, whereas in the other form, they are arranged to form a hexagonal lattice structure. Combination of these poly-types is widely done at the nanoscale level [3]. Despite the process of DLC coating being amorphous, it is quite flexible. The formation of sp^3 is similar to that of the diamond (Figure 1).

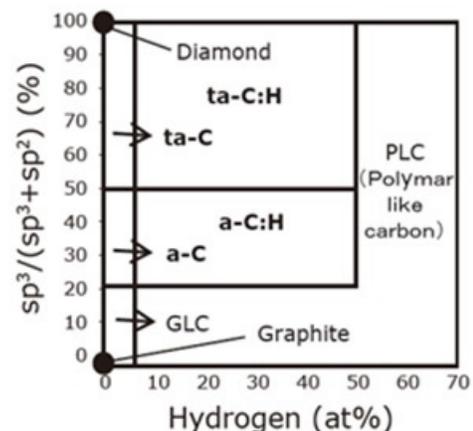


Figure 1: The h value of sp^3 hybridized carbon atoms

The tetrahedral amorphous carbon (ta-C) exhibits a valuable combination of hardness and slickness. A 2-micrometer thickness of the stainless steel coating increases its resistance against abrasive wear, which provides it with longevity spanning from a few weeks to ten years. Ta-C is considered as the purest form of DLC because it is composed of sp^3 bonded carbon atoms. The other six forms of DLC have fillers including hydrogen, sp^2 carbon, and metals that are used to minimize production costs and achieve the desired properties [3,4].

DLC coatings exhibit a great combination of chemical, mechanical, and electrical properties. Compared to conventional hard coatings, DLC coatings can be produced at very low temperatures without compromising hardness [5]. A number of processes can be adopted to produce DLC. These procedures vary with the density of sp^2 and sp^3 atoms. Pressure is applied to forcefully bind the sp^2 with the sp^3 bonds, which lie at a shorter distance. Pressure is also exerted to assure that none of the atoms can revert to their previous position, i.e., the characteristic sp^2 bonds [3].

There have been two methods identified to produce the DLC films [6-10]. Physical Vapor Deposition (PVD) and Chemical Vapor Deposition (CVD). The PVD method makes use of solid (graphite) as the source of producing carbon, whereas the CVD method utilizes gas (hydrocarbon), for instance, methane. The method of laser vapor disposition has been derived from the PVD method and is the most commonly used. The methods such as direct current discharge, self-discharge, and radio frequency are classified as CVD methods.

3. Mechanical Behavior of DLC

3.1. Adhesion

It is necessary for high stress films to be firmly adhered to the implant material, which forms a necessary condition to enable the use of diamond-like carbon. To improve the adhesion of carbon-like metals, intermediate Si layers between the metal and the carbon coating are utilized. The adhesion of diamond-like carbon films on various metallic substrates is due to intermediate layers such as tantalum and chromium.

3.2. Wear

There are multiple processes used for repairing hip and knee joints. Since the movements of orthopedic joints are critically complicated, it is important to consider the wear characteristics of such implants. Joint implants can be easily affected by the tribological environments; therefore, the coatings must be tested for joint stimulators. Ali et al [11] reports that implants made of diamond-like carbon can more typically be applied for tribotesters. Indeed, lubricating environments are the optimal method for stimulating implants and determining their tribological characteristics [11].

3.3. Hardness

Hardness can be described as a measure of the yield stress of a ma-

terial and is measured by a nanoindenter. Hardness is also related to the yield stress and Young's modulus. In diamond-like carbon and other brittle materials, yield occurs whenever a bond splits. Orowan approximation is typically applied to calculate yield stress when a yield occurs, and it assumes that the yield stress is required to break the bonds [11].

3.4. Friction

The friction force results when one surface glides over the other if they share some common points where the concentration of the force is higher. Diamond-like carbon is known for its low friction coefficient. The lubricated friction coefficient of steel on steel is similar to the unlubricated friction coefficient of diamond-like carbon on steel. For a-C:H, the friction coefficient strongly depends on the humidity. Friction coefficient values are found below 0.05 at lower humidity, whereas they increase substantially when the humidity is higher [11].

3.5 Medical Applications of DLC

Biocompatible materials are required to create efficient functioning of the human body. The materials used must exhibit a similar level of sensitivity and functionality as real structures.

3.5.1 Orthopedic Applications of DLC

Sheeja et al [12, 13] conducted some experiments using the cobalt-chromium alloys that compared the 'Ultra-High-Molecular-Weight Polyethylene' (UHMWPE) coated alloy to the uncoated alloy. Simulation was conducted for the fluid flow model that works in the human body. The average wear was found to be identical for both; however, it was noted that the DLC-coated material exhibited ten thousand times less corrosion compared to the uncoated alloy [14].

Love et al [15] compared knee wear with the DLC-coated cobalt-chromium alloy to the uncoated state. The work was performed using simulation programs, and the results revealed that the coated alloy was four times more effective.

3.5.2 Cardiovascular Applications of DLC

Low-Temperature Isotropic (LTI) carbon is the main component of heart valves. Although LTI carbon is manufactured with deliberate care, it is still likely to fail because of breakage that may occur on the surface or subsurface. Since the material is breakable, it has now been replaced with a new hard carbon anticoagulant coating [16-17]. Evaluation of the invitro biocompatibility of DLC-coated stents revealed that the stent coating is important due to the exerted shear forces. The implantation of stents in the coronary artery activates platelets, subsequently resulting in the release of metal ions. This activation triggers thrombosis; therefore, stent coatings remain the favorable approach to prevent this side effect. Studies have revealed that coating intracoronary stents with DLC results in improved biocompatibility and therefore reduces thrombogenicity.

Atomic adsorption spectroscopy has been applied for plasma pro-

cessing in the human body. This process was applied to explore the impacts that the spreading of ions may have on the stents made of metals such as nickel and chromium with or without the DLC coating for 96 hours. Love et al [15] revealed that-coated stents have considerably smaller number of separated ions than uncoated stents. Del Prado et al [14] observed analogous outcomes through the use of an inductively coupled plasma mass spectrometry analysis. This state made it increasingly difficult for the author to evaluate any separation of material ions used for coating stents. It was found that the coated intracoronary stent minimizes the chance of coagulation in addition to reducing severe occlusion and the recurrence of any abnormal narrowing.

The operation conducted at the 'Southwest Research Institute' for coating catheters with DLC also made use of silver. In vitro experiments revealed that DLC coatings protect against bacterial infection [14]. Shi et al [18] measured the compatibility of DLC coatings in the blood, finding a superior possibility of the nonexistence of thrombogenic polymer. It was further found that DLC deserves increased interest for use in the medical field.

4. Diaphragm Penetration

The study examined the use of a micro hardness tester, the AFM, on the deposited DLC films because of R.F. plasma discharge. It is apparent that the roughness and hardness of the films depend upon the bias voltage provided to the substrates and upon the pressure exerted in the deposition chamber. The roughness of DLC film surface increases in the deposition with the level of pressure. A decrease in roughness has been observed at a pressure level below 53 Pa, but hard films are obtained.

Different coating parameters are applied when working with DLC materials, and the exertion of pressure forms an essential act of coating the substrate. The different options available for pressure include 13 Pa, 53 Pa, and 153 Pa [18]. Generally, 13 Pa is considered the ideal option for coating the substrate because it leads to harder films with low rates of deposition and yields the purest carbon compared to the other options. There is a clear relationship between the higher hardness rates of DLC films and the lower rates of deposition.

There was a problem observed regarding platelet adhesion with blood in an experiment conducted similar to that of Gutensohn et al [17]. An unforeseen increase in platelet adhesion was observed when the 13 Pa pressure was applied. This pressure resulted in coagulation of blood.

There was also an increase in heat on the electrodes and platelet adhesion with the blood substrate, which formed various cracks in the DLC surface. Based on these findings, it can be stated that blood will approach the coated substrate [18].

It was further observed that the increase in electrode heat resulted because higher bias voltages were applied.

It has further been observed that the duration of the deposition time created additional problems. This can be observed where an increase in the rate of platelet adhesion occurred when a 13 Pa pressure was applied [18,19].

To solve this problem, initially, there should be a solution to prevent the electrode from heating. This emphasizes the need of an appropriate cooler that can be placed under the electrode.

5. Investigating the Functionality of DLC Films on an Artificial Heart Diaphragm

5.1 Deposition and Diffusion

Artificial hearts contain a power adapter, blood type diaphragm, two oval pumps, and multiple electronic modules. The power adapter plays an important role in delivering hydraulic silicone oil into the blood as it is pumped through a pair of oil channels. The rotating pulse of silicone oil makes circulation more flexible. The diaphragm is composed of synthetic polyurethane rubber that splits the silicone oil and blood into the chamber. In the whole system, the permeation of silicon oil through the diaphragm constitutes a serious issue. This is because the penetration may undermine the device's hydraulic function. Furthermore, this permeation can result in the accumulation of silicone oil and cause toxic effects. (Figure 2.1.1) shows an elliptical pump and diaphragm [20].

(Figure 2.1.2) shows the samples placed between the two visible cells. In the given experimental system, the physiologic saline and distilled water have been used to fill each cell. Moreover, Induced Plasma Mass Spectroscopy (MIPMS) is applied for measuring the Na ions in the distilled water [20-22].

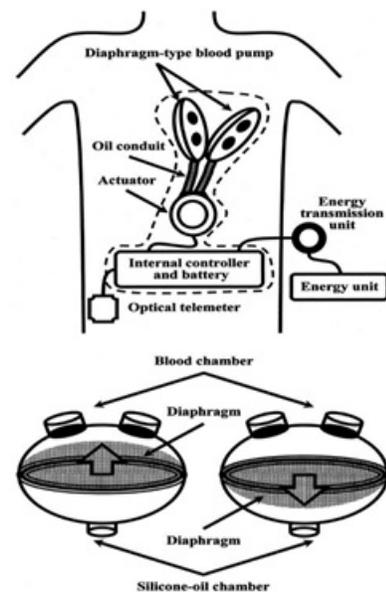


Figure 2.1.1: An elliptical pump and diaphragm

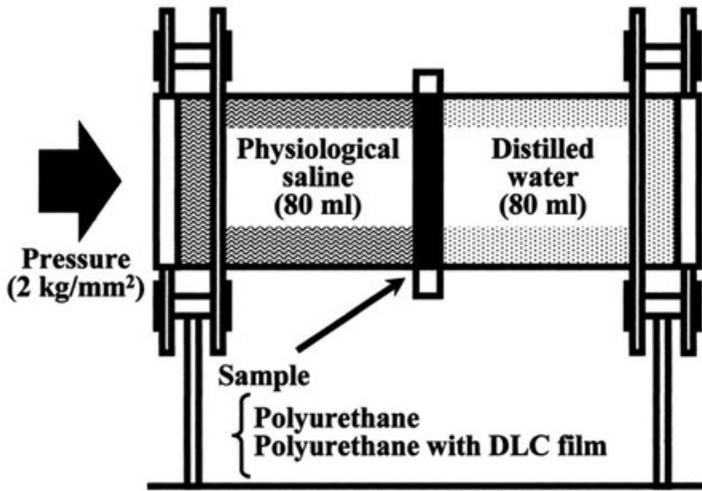


Figure 2.1.2: An experimental system with two visible cells

The table below shows the total quantity of the Na₊ ions that penetrated the polyurethane and reached the distilled water. Prior to the experiment, the initial concentration of Na₊ ions was found to be 1.25 ppb in the distilled water. However, the concentration of Na₊ ions rose to 32.8 ppm when a 2 kg/mm² static pressure was applied; this was done with an uncoated sample, i.e., without a DLC film. In contrast, the concentration of Na₊ ions was found to be 1 ppb in the distilled water with the DLC films. Considering this difference, it can be stated that Na₊ ions showed no penetration with the use of the sample coated with DLC films [11].

5.2 Production of DLC Films on an Ellipsoidal Substrate Surface

The use of planar electrodes is the most popular method of operation when RF plasma is used. Therefore, it is not easy to uniformly deposit the DLC film upon the surfaces of an insulator material, especially when a three-dimensional shape is used. To solve this issue, a unique electrode has been developed as shown in (Figure 2.2.1). An ellipsoidal substance is used with an improved electrode for the efficient conduction of ions. Ohgoe et al [21,22] identified this method as a useful process for achieving the desired thickness of the DLC films along with structural improvements in the electrode as well as in the film.

Silicon wafers are used to examine the uniformity of DLC films using the effective electrode operation. (Figure 2.2.2) shows silicon wafers placed at different positions on the effective electrode surface [20,21].

(Figure 2.2.3) shows that the diamond-like carbon film thickness is intricately linked with the four different positions using an improved electrode process. The use of an improved electrode keeps the thickness of DLC films uniform at the same unit. However, it remained difficult to prove uniformity of the DLC film using the conventional process. This subsequently results in clear evidence that the use of an improved electrode process positively impacts the rate of deposition.

An in vitro testing method was applied for twenty days to the system, and the DLC film on the diaphragm surface was examined under the process of pulsation. (Figure 2.2.4) shows the amount of silicone oil through the diaphragm. The penetration of silicone oil was decreased to 1/3 by using the DLC film coating compared to the uncoated surface [21].

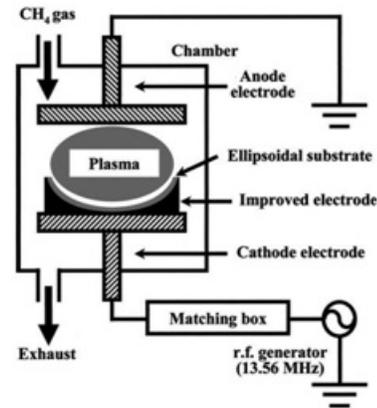


Figure 2.2.1. An improved system for the efficient deposition of DLC films for three-dimensional shapes

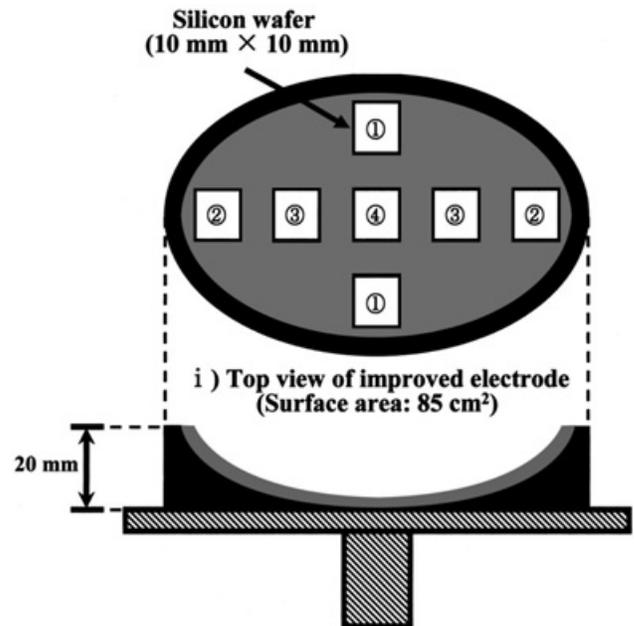


Figure 2.2.2: The effective electrode operation

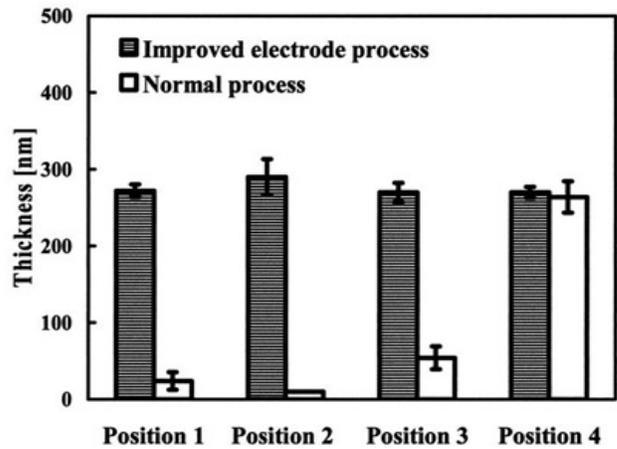


Figure 2.2.3: An improved electrode process

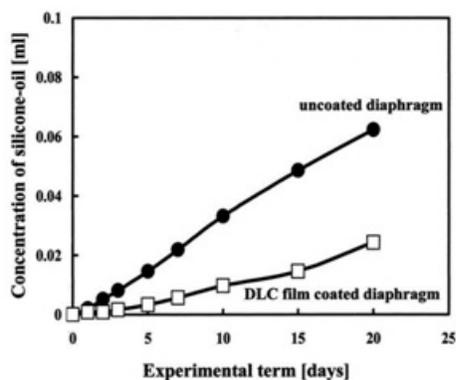


Figure 2.2.4: The penetration of silicon oil

5.3 Conclusion and Summary

DLC films are used for coating ellipsoidal diaphragms (polyurethane elastomer) and hence form an influential biomaterial for the functioning of artificial hearts. Such coatings are used to prevent penetration of the hydraulic silicone oil through the diaphragm into the blood. In vitro testing was conducted to estimate the penetration of the silicone oil through the diaphragm, with the pressure of silicone oil varying accordingly. The process was conducted over a period of 20 days. In this in vitro test, successful attachment of uniform deposition of the diamond-like carbon film was achieved on the ellipsoidal diaphragm, and the diamond-like carbon film exhibited good stability. The amount of silicone oil penetration improved by one-third using the diamond-like carbon film coating compared to the uncoated diaphragm. It is expected that the use of the diamond-like carbon film may increase the dynamic compatibility of an artificial heart.

The artificial heart forms a specific intervention that can be used to treat various heart diseases. Silicon oil is used as a pillar for the artificial heart. However, certain problems may arise with silicon oil ions as they diffuse into the blood through ion penetration. There are seven forms of Diamond-Like Carbon (DLC), and all forms have a high value of sp^3 hybridized carbon atoms. DLC can be found in more than one type, primarily because the diamond is produced in two different crystalline poly-types. DLC coatings exhibit a valuable combination of chemical, mechanical, and electrical properties. Compared to conventional hard coatings, DLC coatings can be produced at very low temperatures without compromising hardness. The study examined the use of a micro hardness tester, the AFM, and the DLC films deposited because of R.F. plasma discharge. It is apparent that the roughness and hardness of films depend upon the bias voltage provided to the substrates and upon the pressure exerted in the deposition chamber. Artificial hearts contain a power adapter, blood type diaphragm, two oval pumps, and multiple electronic modules. The power adapter plays an important role in delivering hydraulic silicone oil into the blood as it is pumped through a pair of oil channels. The rotating pulse of silicone oil makes the circulation more flexible. The use of planar electrodes is the most popular method of operation when RF

plasma is used. Therefore, it is not easy to uniformly deposit the DLC film upon the surfaces of insulator material, especially when a three-dimensional shape is used. DLC films are used for coating ellipsoidal diaphragms (polyurethane elastomer) and hence are an influential biomaterial for the functioning of artificial hearts. Such coatings are used to prevent the penetration of the hydraulic silicone oil through the diaphragm into blood.

Table 1: The quantity of Na^+ ions penetration (1 ppm = $1/10^6$ and 1 ppb = $1/10^9$)

Diffusion Concentrations of Distilled Water Through the DLC Film	
Substrates	Na^+ ion in the distilled water cell
DLC film (deposition at 30 Pa)	1.13 ppb
DLC film (deposition at 50 Pa)	0.76 ppb
DLC film (deposition at 100 Pa)	0.85 ppb
Polyurethane (without DLC film)	32.8 ppm

5.4 Future Trends

The significance of DLC has led researchers to search for materials that can be applied to make interventions more effective and discipline oriented. DLC applications have increased and are now being applied on a wider scale. DLC is commercially utilized for coating because of its low cost and the convenience of the unique properties it provides for many demands. Thin layer coatings have been applied for the last 20 years for solid lubrication and have reached the limit of usable materials. Extension of modern features for use with thin coatings is needed because of increased demand for an appropriate environment for lubricants. Comparable tests have also validated the performance and strength of DLC films [23]. However, more efforts can be made to improve and develop the lubricated sliding status. There is a need for unique structures that can be used as reliable sliding surfaces. The study suggests the need for extending research on DLC deposition mechanisms and mechanisms to improve the adhesion of platelets. Moreover, efforts must be made to improve the deposition method of DLC, and the biocompatibility features of DLC must also be investigated to vary the depth.

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