Chapter 13

Diamond-Like Carbon Coatings for Joint Arthroplasty

So Nagashima, Myoung-Woon Moon and Kwang-Ryeol Lee

Institute for Multidisciplinary Convergence of Matter,
Korea Institute of Science and Technology, Seoul, Korea

1. Introduction

With the increase in the average human lifespan, there is an increased demand for high quality health-related products. Biomedical implants such as hip joints, vascular grafts, and dental roots have proven to be effective for the treatment of major injuries to improve the overall quality of life. Joint replacement is a common orthopedic procedure wherein dysfunctional joints, including hips and knees, are replaced with implants. These implants are primarily composed of metals (e.g. titanium, stainless steel), metal alloys (e.g. titanium–aluminum–vanadium alloys, cobalt–chromium–molybdenum alloys), ceramics (alumina-based), or polymeric materials (e.g. ultra-high molecular weight polyethylene (UHMWPE)). Such implants demonstrate adequate short-term biocompatibility and mechanical properties; however, they are far from being completely biostable or inert. Accordingly, these implants suffer from several drawbacks with respect to long-term use, such as cytotoxicity to surrounding tissues, the release of metal ions or wear debris that causes allergic reactions, corrosion, and frictional wear. To reduce such risks, the biological compatibility and long-term stability of joint replacement implants need to be improved.
Surface properties significantly affect the overall performance of implants, and surface modification with biologically, mechanically, and chemically stable materials is an effective method for overcoming the aforementioned drawbacks. Diamond-like carbon (DLC) is an amorphous carbon that possesses outstanding properties, including high hardness, a low friction coefficient, chemical inertness, high wear, and corrosion resistance, and biological compatibility. Since Aisenberg and Chabot (1971) first reported the synthesis of DLC, it has gained considerable attention as a functional coating material, and its biomedical applications have been actively explored, including coatings for hip and knee implants to prevent or minimize wear, inhibit corrosion, and maintain biological compatibility. Wear debris from joint implants can induce adverse biological reactions and cause bone loss and implant loosening. Therefore, the wear behavior of implants should be carefully examined. This chapter includes a brief, fundamental introduction to DLC, a review of recent studies on the evaluation of wear performance of various DLC joint implant coatings, and a discussion on issues to be solved for the effective development of DLC-coated implants with satisfactory performance.

2. DLC

DLC is an amorphous carbon comprising a mixture of $sp^3$ and $sp^2$ carbon bonds with various levels of hydrogen. Owing to its attractive properties, DLC has attracted a great deal of attention as a promising material for use in a range of applications. DLC can be synthesized by a variety of methods, and its properties can be controlled by altering the synthesis method and parameters. This allows one to synthesize DLC with the properties required for a particular application by selecting the appropriate synthesis method and optimizing the parameters. In this section, the fundamental properties of DLC will be described, with an explanation of approaches to tuning them.

2.1. Deposition Methods and Fundamental Properties

A number of techniques based on physical vapor deposition (PVD) or chemical vapor deposition (CVD) have been developed for the
synthesis of DLC, including filtered cathodic vacuum arc (FCVA), ion plating, plasma immersion ion implantation and deposition (PIIID), magnetron sputtering, ion beam sputtering, pulsed laser deposition, and radio frequency plasma enhanced CVD (r.f.-PECVD) (Cuong et al., 2003; He et al., 1994; Leu et al., 2004; Sánchez et al., 2000; Shim et al., 2000; Sui et al., 2006; Zou et al., 2004). Figure 13-1 shows schematics of representative systems for the synthesis of DLC (Robertson, 2002), and detailed explanations of the systems can be found in the corresponding reference. The properties of DLC vary based on the synthesis method and parameters. The precise control of the synthesis parameters directly affects the chemical structure of DLC, such as the $sp^3:sp^2$ ratio and hydrogen content, to produce DLC with properties that range from polymer like to diamond like.

As shown in Figure 13-2, there are various forms of amorphous carbon. DLC is the general term used to describe a broad range of amorphous carbon that can be categorized into several types according to its properties (Robertson, 2002). Amorphous carbon (a-C) has a high $sp^3$ bond content (40–80%), and hydrogenated amorphous carbon (a-C:H) contains up to approximately 40% $sp^3$ bonds (Donnet et al., 1999). Tetrahedral amorphous carbon (ta-C) is a type of a-C with a significant quantity of $sp^3$ bonds (>70%) (McKenzie, 1996). The fraction of $sp^3$ bonds in amorphous carbon is closely related to the mechanical properties, including hardness, elastic modulus, and residual stress. The hardness of ta-C measures as high as 80 GPa, and that of a-C:H is in the range 10–30 GPa (Robertson, 1992). Although the friction coefficient of a-C:H is reportedly lower than that of ta-C in dry conditions, the wear rate for a-C:H is higher than that for ta-C in various testing conditions (Erdemir and Donnet, 2006). The residual stress in DLC is an intrinsic nature and is strongly correlated with the kinetic energy of the deposited carbon atoms, which is dependent on the bias voltage, pressure, and precursor gas molecules (Lee et al., 1994). When the stress in a DLC film deposited on a substrate exceeds the interfacial adhesion strength, the film can delaminate from the substrate, which eventually degrades the overall performance. Thus, residual stress should be lowered, which can be accomplished by incorporating an appropriate third element, such as
Si or Ti, into the film or depositing an interlayer onto the substrate prior to film deposition.

The biological properties, including hemocompatibility and cell compatibility, of DLC have been actively studied in *in vitro* and *in vivo* systems for biomedical applications, and numerous researchers
Figure 13-2. Ternary phase diagram of amorphous carbon materials (Robertson, 2002). Reprinted with permission from Elsevier.

have reported its excellent biocompatibility. For example, Mohanty et al. (2002) implanted bare Ti substrates, commercially used biomaterials, and DLC-coated Ti substrates in the skeletal muscle of rabbits and investigated the surrounding tissue response. DLC was synthesized by r.f.-PECVD, and the specimens were explanted after 1, 3, 6, and 12 months. The results from this study demonstrated that the DLC-coated substrates were as biocompatible as the uncoated substrates, even after long-term implantation, indicating the good biocompatibility of DLC.

2.2. Incorporation of a Third Element

Several attempts have been made to further improve the properties of DLC. The amorphous nature of DLC allows for incorporation of a third element, such as Si (Jones et al., 2010; Kim et al., 2005; Lee et al., 1997, 2002; Maguire et al., 2005; Ogwu et al., 2008; Okpalugo et al., 2004; Papakonstantinou et al., 2002), F (Hasebe et al., 2006, 2007; Saito et al., 2005), P (Kwok et al., 2005), Ag (Ahmed et al., 2009; Choi et al., 2007, 2008; Kwok et al., 2007), N (Okpalugo et al., 2008; Yokota et al., 2007), or Ti (Bui et al., 2008; Gilmore and Hauert, 2001; Ouyang and Sasaki, 2005; Pandiyaraj et al., 2012), the concentration of which significantly affects the resulting DLC properties. For example, Choi et al. (2007) prepared Ag-incorporated DLC films using ion beam...
deposition and investigated the effect of the Ag content on the residual stress. Their results demonstrated that increasing the Ag content up to 9.7 at. % resulted in a decrease in stress from >3.0 to 1.3 GPa, indicating that the residual stress was strongly dependent on the Ag content. Lee et al. (2002) synthesized ta-C films using a filtered vacuum arc of graphite with simultaneous sputtering of Si and measured the residual stress as a function of the varied Si content. They reported that the residual stress decreased from 6.0 to 3.3 GPa by incorporating 1 at. % of Si, and further increases in the Si content to 50 at. % resulted in stress decreases to 0.8 GPa. The incorporation of a third element also changes the biological compatibility of DLC. Saito et al. (2005) synthesized F-incorporated DLC (F-DLC) using an r.f.-PECVD apparatus and demonstrated that F-DLC dramatically suppressed platelet adhesion and activation compared with DLC alone. Ogwu et al. (2008) prepared Si-incorporated DLC (Si-DLC) using an r.f.-PECVD system and showed the improved adhesion of human microvascular endothelial cells compared with unmodified DLC.

3. Wear Behavior

The wear debris released from joint implants can induce adverse biological reactions and cause both bone loss and implant loosening. Therefore, the wear behavior of the implants should be carefully examined, and the wear properties of DLC-coated joint implants have been studied in vitro using several different methods, including pin-on-disk, hip joint simulators, and self-made simulators (Affatato et al., 2000; Dong et al., 1999; Dowling et al., 1997; Fisher et al., 2004; Lappalainen et al., 1998, 2003; Oñate et al., 2001; Platon et al., 2001; Saikko et al., 2001; Sheeja et al., 2001; Shi et al., 2003; Thorwarth et al., 2010; Tiainen, 2001; Xu and Pruitt, 1999).

3.1. Pin-On-Disk

Pin-on-disk is the most commonly used method for evaluating wear behavior, wherein a flat or sphere-shaped indenter is located on a test plate with a precisely known force and the wear coefficients for the pin and the plate are calculated from the volume of material lost.
during a given friction run. Several parameters can be controlled in this process, including contact pressure, temperature, humidity, and lubrication. This method provides basic information on the properties and tribological performance of materials. Hip prostheses are ball-in-socket joints that consist of an acetabular cup (socket) that is usually made of UHMWPE and a femoral head that is made of metallic alloys (e.g. CoCr) or ceramics (e.g. \( \text{Al}_2\text{O}_3 \)). DLC coatings have been applied to the materials used for the femoral head of hip prostheses. Comparative tribological tests using ball-on-disk and pin-on-disk methods have been developed to investigate the wear of different materials used for hip joint prostheses. Platon et al. (2001) compared the wear rate of stainless steel, titanium alloy, alumina, zirconium dioxide, DLC-coated stainless steel, and DLC-coated titanium and demonstrated the superior wear resistance of the DLC-coated materials. The DLC coating was prepared using a PECVD method in that study, but no detailed description of the process was provided. Lappalainen et al. (1998) prepared DLC-coated substrates, including CoCrMo and Ti$_6$Al$_4$V, using a filtered pulsed arc discharge method and investigated the wear resistance of UHMWMPE with a NaCl solution as a lubricant. The resistance was found to be improved by a factor of up to 600 (Lappalainen et al., 1998). Conversely, Sheeja et al. (2001) evaluated the wear properties of DLC-coated CoCrMo against UHMWPE, where the DLC coating was synthesized using a FCVA, and found no favorable improvement in the wear behavior of the DLC-coated specimen (Table 13-1). Sheeja et al. (2005) conducted a study on the tribological properties of DLC-coated CoCrMo using a pin-on-disk method in simulated body fluid, where the DLC coating was fabricated using the filtered cathodic vacuum arc method, and found that coating the surface of both UHMWPE and CoCrMo with DLC enhanced the lifetime of the implants to a considerable extent.

### 3.2. Joint Simulators

Simulators have also been widely utilized to investigate the performance of DLC-coated specimens. Lappalainen et al. (2003) performed a study on DLC-coated hip joints using a commercially available hip joint simulator, where the DLC coating was prepared
Table 13-1. The short- and long-term tribological behavior of DLC-coated and uncoated CoCrMo alloys sliding against UHMWPE in simulated body fluid evaluated using a pin-on-disk tribometer (Sheeja et al., 2001). Reprinted with permission from Elsevier.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test condition</th>
<th>No. of cycles</th>
<th>Friction coefficient</th>
<th>Wear of UHMWPE pin (mm$^3$/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Uncoated</td>
<td>Load = 10 N</td>
<td>30 000</td>
<td>0.08 ± 0.01</td>
<td>4.97 × 10$^{-7}$</td>
</tr>
<tr>
<td>Co–Cr–Mo alloy</td>
<td>Speed = 6 cm/s</td>
<td>120 000</td>
<td>0.05 ± 0.00</td>
<td>1.65 × 10$^{-7}$</td>
</tr>
<tr>
<td></td>
<td>Environment = SBF Track radius = 8 mm</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DLC coated</td>
<td>Load = 10 N</td>
<td>30 000</td>
<td>0.17 ± 0.02</td>
<td>5.31 × 10$^{-7}$</td>
</tr>
<tr>
<td>Co–Cr–Mo alloy</td>
<td>Speed = 6 cm/s</td>
<td>120 000</td>
<td>0.14 ± 0.01</td>
<td>2.02 × 10$^{-7}$</td>
</tr>
<tr>
<td></td>
<td>Environment = SBF Track radius = 8 mm</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

by filtered pulsed plasma arc discharge. This study revealed that the wear rates measured for 15 million walking cycles, corresponding to approximately 15 years of clinical use, in serum lubrication were 10$^6$ times lower than the clinical values for conventional metal-on-metal or UHMWPE-on-metal pairs (Lappalainen et al., 2003). Tiainen (2001) used a hip simulator to study the mechanical properties of ta-C coatings prepared with filtered pulsed arc discharge for biomechanical applications. The wear of ta-C coated metal-on-polyethylene joints was found to be 10$^5$–10$^6$ times smaller than metal-on-polyethylene or metal-on-metal joints. Dowling et al. (1997) evaluated the wear performance of DLC-coated orthopedic implants, where DLC films with 40–50% sp$^3$ content were synthesized using a saddle beam deposition system. The stainless steel femoral head coated with the DLC film showed a significantly lower level of UHMWPE wear after 6 million cycles compared with the uncoated femoral head. Saikko et al. (2001) conducted a study on the wear of polyethylene acetabular cups against CoCr, alumina, and DLC-coated CoCr using a hybrid vapor deposition process with a biaxial hip wear simulator and diluted calf serum as the lubricant. Figure 13-3 shows scanning electron microscopic (SEM) images of
Figure 13-3. SEM images of the bearing surface of polyethylene acetabular cups used in a hip wear simulator for 3 million cycles against (a) alumina, (b) CoCr, and (c) DLC-coated heads, and (d) used in vivo for 97 months against a CoCr head (Saikko et al., 2001). Each scale bar section in (d) corresponds to 10 µm. Reprinted with permission from Elsevier.

the bearing surface of a polyethylene acetabular cup tested in the hip wear simulator for 3 million cycles against (a) alumina, (b) CoCr, and (c) DLC-coated heads and a polyethylene acetabular cup after (d) 97 months in vivo against a CoCr head. Figure 13-4 presents SEM images of polyethylene wear particles produced against (a) alumina, (b) CoCr, and (c) DLC-coated heads. Although the authors noted that the wear resistance of the DLC coating did not markedly differ from those of CoCr and alumina against polyethylene, detailed information on the DLC coating was not provided in the study, which prevents a careful interpretation of their results.
3.3. **Self-Made Simulators**

Wear behavior should be evaluated under conditions that resemble *in vivo* situations; to this end, self-made simulators have been employed to evaluate DLC-coated specimen performance (Oñate *et al.*, 2001; Thorwarth *et al.*, 2010). Oñate *et al.* (2001) used a special knee wear simulator to investigate the wear performance of UHMWPE plates against DLC-coated CoCr and Al$_2$O$_3$ balls. The simulator was used with a combined rolling-sliding movement that corresponded to the most unfavorable wear situation in the knee. The DLC film in this study was synthesized by r.f. glow discharge of C$_2$H$_2$ gas, and the coated and uncoated samples were tested against UHMWPE.

Figure 13-4. SEM images of polyethylene wear particles produced in a hip wear simulator against (a) alumina, (b) CoCr, and (c) DLC-coated heads (Saikko *et al.*, 2001). Reprinted with permission from Elsevier.
Table 13-2. Weight loss of UHMWPE tested in a knee wear simulator at 5 million wear cycles (Oñate et al., 2001). Asterisks indicate contacting materials with statistically significant differences. Reprinted with permission from Elsevier.

<table>
<thead>
<tr>
<th>Test No.</th>
<th>Ball material (femoral head)</th>
<th>Plate material</th>
<th>Average UHMWPE wear (mg)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Co–Cr–Mo</td>
<td>UHMWPE</td>
<td>−0.690*</td>
<td>0.078</td>
</tr>
<tr>
<td>2</td>
<td>Co–Cr–Mo coated with TiN</td>
<td>UHMWPE</td>
<td>−3.531**</td>
<td>0.330</td>
</tr>
<tr>
<td>3</td>
<td>Co–Cr–Mo treated with N+ implantation</td>
<td>UHMWPE</td>
<td>−0.130</td>
<td>0.049</td>
</tr>
<tr>
<td>4</td>
<td>Co–Cr–Mo coated with DLC</td>
<td>UHMWPE</td>
<td>−0.150</td>
<td>0.090</td>
</tr>
<tr>
<td>5</td>
<td>Co–Cr–Mo treated with N+ implantation</td>
<td>UHMWPE</td>
<td>−0.244</td>
<td>0.183</td>
</tr>
<tr>
<td>6</td>
<td>Ceramic Al₂O₃</td>
<td>UHMWPE</td>
<td>−0.253</td>
<td>0.002</td>
</tr>
</tbody>
</table>

plates. This study revealed that the DLC coating led to a reduction in UHMWPE wear at up to 5 million wear cycles, representing approximately 3 years of implant life (Table 13-2). Thorwarth et al. (2010) employed a simulator that induced a simplified spinal motion for the evaluation of wear performance of DLC-coated ball-on-socket implant pairs made from Co₂₈Cr₆Mo. The DLC coating was prepared with an r.f.-PECVD system using C₂H₂ gas, and the DLC-coated pairs and uncoated reference samples were subjected to wear tests in a simplified linear spinal simulator setup. The authors found that uncoated samples began to generate metal wear after 7 million loading cycles, with the wear volume eventually exceeding 20 times that of the DLC-coated samples (Figure 13-5). This volume corresponds to approximately two to three years in vivo, which demonstrates a significant improvement in wear resistance.

4. Delamination

Delamination is the instability of the coating layer that is commonly observed in DLC-coated specimens, which impairs their overall
performance and long-term stability. The high residual stress of DLC and poor substrate adhesion are implicated in early delamination. Thus, lowering the residual stress by incorporating a third element, such as Si or Ti, or depositing an interlayer has attracted much attention as a method for reducing delamination. Specifically, a thin layer of amorphous hydrogenated silicon or amorphous silicon has been used as an interlayer between Ti$_6$Al$_4$V substrates and DLC or Si-DLC to promote improved adhesion (Chandra et al., 1995a, 1995b; Kim et al., 2005, 2008). Although these interlayers appear to work effectively in vitro, they do not necessarily ensure long-term performance in vivo. Recently, delamination that occurs many years after implantation has been the focus of in-depth discussion (Hauert et al., 2012a, 2012b, 2013). This delayed delamination can be ascribed to slow corrosion processes related to the crevice corrosion (CC) of a Si-based interlayer and the stress corrosion cracking (SCC) of a reactively formed interface. The in vitro testing methods that are commonly used prior to implantation only evaluate the wear properties and cannot approximate the corrosion properties of the interlayer or the reactively formed interface, which hinders an
accurate understanding of the \textit{in vivo} behavior. Delayed delamination is considered a serious issue in developing DLC-coated joint implants. Therefore, detailed investigations on the properties of the interlayer and interface should be carefully performed to better guarantee the long-term \textit{in vivo} stability of these implants.

5. Concluding Remarks

DLC possesses outstanding physical and biological properties and has thus been a focus of active research for the development of highly functionalized joint implants. Here, the wear properties of DLC-coated specimens have been discussed. Many research groups have performed \textit{in vitro} and \textit{in vivo} studies and reported that DLC coatings can significantly reduce implant wear, suggesting that DLC coatings can be effectively applied to conventional joint implants. However, it should be noted that several important issues hinder the practical application of DLC coatings. First, there is no well-established, standardized procedure for evaluating the coating properties. Thus, researchers must determine the experimental methods and conditions independently. Their results can be affected by the properties of the coating and by the chosen experimental setup, and it is therefore difficult to directly compare data among different groups and to properly judge the efficiency of their respective DLC coatings. Second, the properties of DLC coatings are widely varied. Although these properties are largely dependent on the synthesis method and parameters, detailed information on DLC coating properties is not typically provided in studies. This inconvenience also significantly hinders the direct comparison of data presented by different groups. Finally, DLC coatings can spontaneously delaminate from their substrates. Such delamination not only negates the beneficial effects of the coatings but also further degrades the implants. This issue becomes especially significant after long-term use. The aforementioned drawbacks should be addressed in future research to promote the effective use of DLC coatings in joint implants.

The current situation provides information on the importance of careful interpretation of the reported results and the necessity of developing a universal experimental procedure for accurately
predicting *in vivo* performance. In addition, although the focus of this chapter has been on the wear behavior of DLC-coated specimens, corrosive and biological properties should also be carefully examined. Comprehensive assessment and precise understanding of the *in vivo* properties are vital to the successful development of DLC-coated implants.

**References**


