Chapter 13

Diamond-Like Carbon Coatings for Joint Arthroplasty

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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

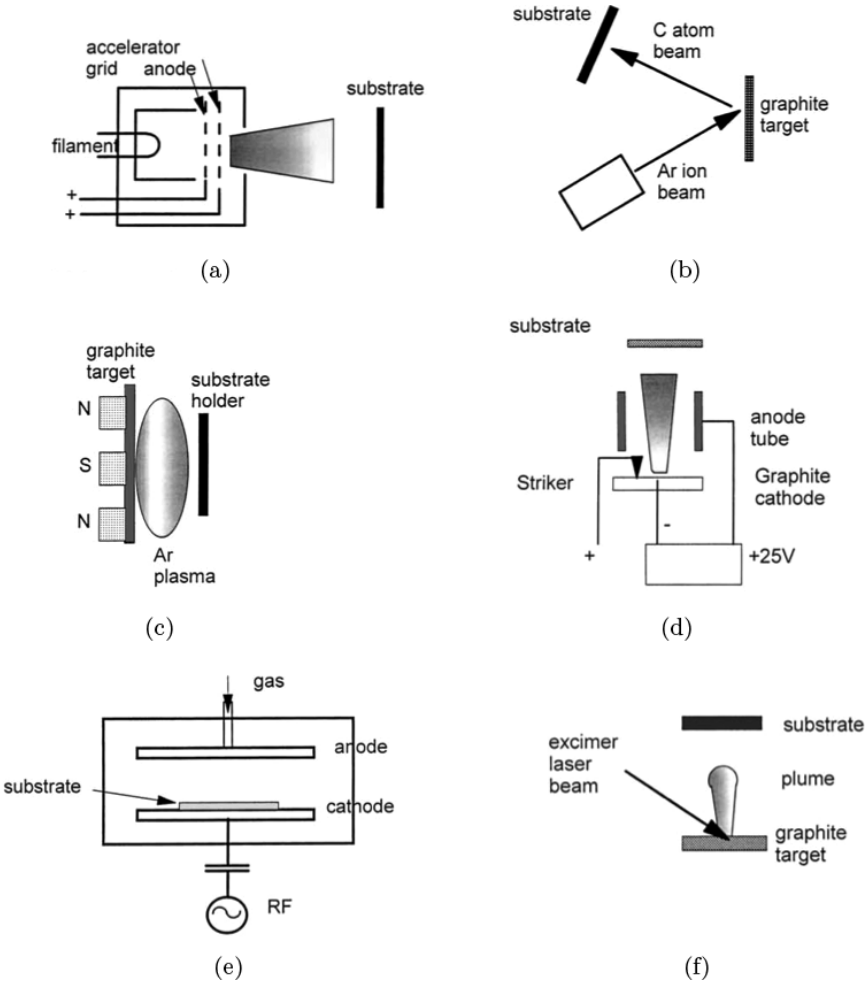

Figure 13-1. Schematics of representative systems for the synthesis of DLC (Robertson, 2002). Reprinted with permission from Elsevier. (a) Ion deposition, (b) Ion assisted sputtering, (c) Sputtering, (d) Cathodic Vacuum Arc, (e) Plasma deposition, (f) Pulsed laser deposition.

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

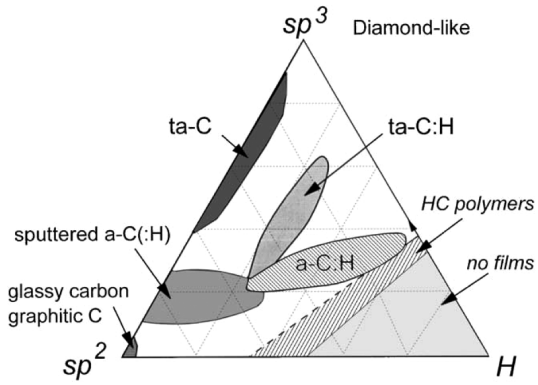

Figure 13-2. Ternary phase diagram of amorphous carbon materials (Robertson, 2002). Reprinted with permission from Elsevier.

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. Al_2O_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_6Al_4V, using a filtered pulsed arc discharge method and investigated the wear resistance of UHWMPE 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.

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

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

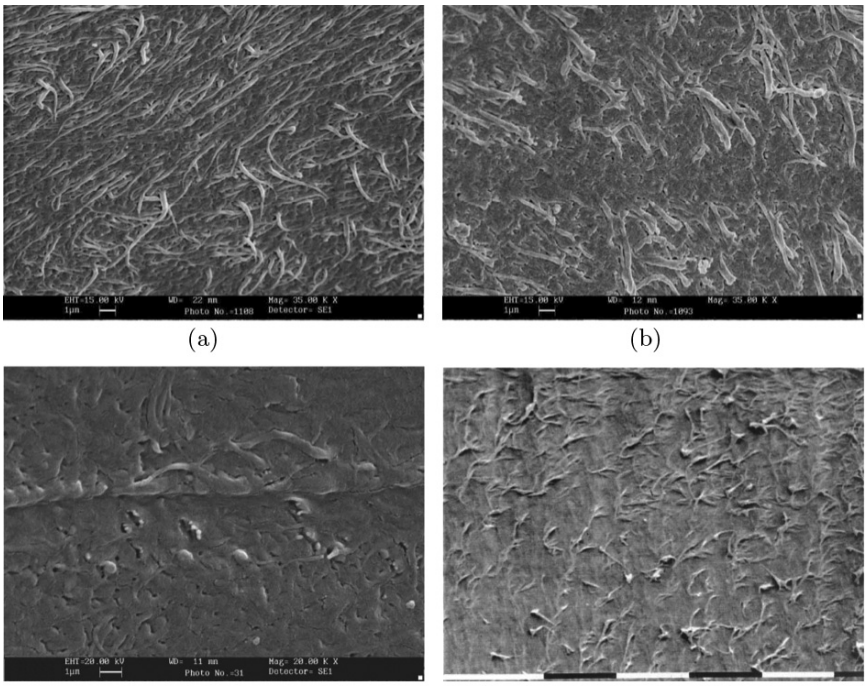

Figure 13-3. SEM images of the bearing surface of polyethylene acetabular cups used in a hip wear simulator for 3 million cycles against (a) alumina, (b) CoCr, and (c) DLC-coated heads, and (d) used *in vivo* for 97 months against a CoCr head (Saikko *et al.*, 2001). Each scale bar section in (d) corresponds 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.

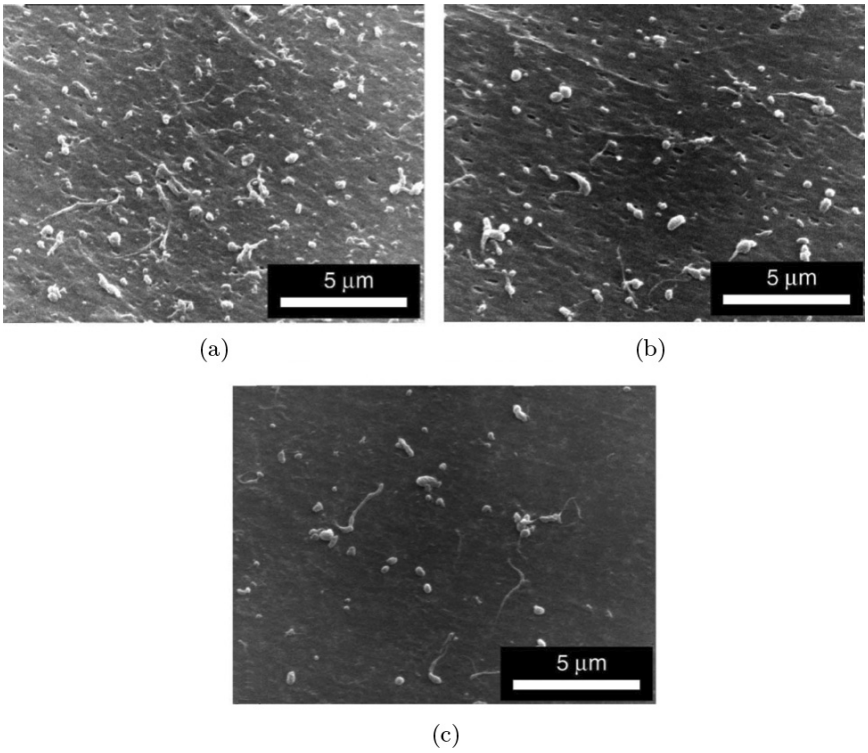

Figure 13-4. SEM images of polyethylene wear particles produced in a hip wear simulator against (a) alumina, (b) CoCr, and (c) DLC-coated heads (Saikko *et al.*, 2001). Reprinted with permission from Elsevier.

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_2O_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_2H_2 gas, and the coated and uncoated samples were tested against UHMWPE

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.

Test No.	Ball material (femoral head)	Plate material	Average UHMWPE wear (mg)	Standard deviation
1	Co–Cr–Mo	UHMWPE	-0.690^{*}	0.078
2	Co–Cr–Mo coated with TiN	UHMWPE	-3.531^{**}	0.330
3	Co–Cr–Mo treated with N^+ implantation	UHMWPE	−0.130	0.049
4	Co–Cr–Mo coated with DLC	UHMWPE	−0.150	0.090
5	Co–Cr–Mo	UHMWPE treated with N^+ implantation	−0.244	0.183
6	Ceramic Al_2O_3	UHMWPE	−0.253	0.002

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 $Co_{28}Cr_6Mo$. The DLC coating was prepared with an r.f.-PECVD system using C_2H_2 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

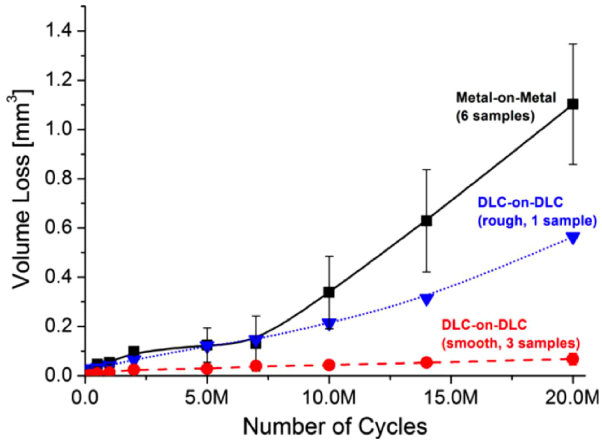

Figure 13-5. Wear volumes for metal-on-metal and smooth and rough DLC-on-DLC pairs tested in protein-containing simulated body fluid (Thorwarth *et al.*, 2010). The load and motion frequency were 1200 N and 3 Hz, respectively. Reprinted with permission from Elsevier.

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_6Al_4V 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 *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 *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 *in vitro* and *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

Affatato, S., Frigo, M. and Toni, A. (2000). An *in vitro* investigation of diamond-like carbon as a femoral head coating, *J Biomed Mater Res*, **53**, 221–226.

Ahmed, S.F., Moon, M.W. and Lee, K.R. (2009). Effect of silver doping on optical property of diamond like carbon films, *Thin Solid Films*, **517**, 4035–4038.

Aisenberg, S. and Chabot, R. (1971). Ion-beam deposition of thin films of diamondlike carbon, *J Appl Phys*, **42**, 2953–2958.

Bui, X.L., Pei, Y.T. and De Hosson, J.T.M. (2008). Magnetron reactively sputtered Ti-DLC coatings on HNBR rubber: the influence of substrate bias, *Surf Coat Tech*, **202**, 4939–4944.

Chandra, L., Allen, M., Butter, R., Rushton, N., Lettington, A.H. and Clyne, T.W. (1995a). The effect of biological-fluids on the adhesion of diamond-like carbon-films to metallic substrates, *Diam Relat Mater*, **4**, 852–856.

Chandra, L., Allen, M., Butter, R., Rushton, N., Lettington, A.H. and Clyne, T.W. (1995b). The effect of exposure to biological-fluids on the spallation resistance of diamond-like carbon coatings on metallic substrates, *J Mater Sci Mater M*, **6**, 581–589.

Choi, H.W., Choi, J.H., Lee, K.R., Ahn, J.P. and Oh, K.H. (2007). Structure and mechanical properties of Ag-incorporated DLC films prepared by a hybrid ion beam deposition system, *Thin Solid Films*, **516**, 248–251.

Choi, H.W., Dauskardt, R.H., Lee, S.C., Lee, K.R. and Oh, K.H. (2008). Characteristic of silver doped DLC films on surface properties and protein adsorption, *Diam Relat Mater*, **17**, 252–257.

Cuong, N.K., Tahara, M., Yamauchi, N. and Sone, T. (2003). Diamond-like carbon films deposited on polymers by plasma-enhanced chemical vapor deposition, *Surf Coat Tech*, **174**, 1024–1028.

Dong, H., Shi, W. and Bell, T. (1999). Potential of improving tribological performance of UHMWPE by engineering the Ti_6Al_4V counterfaces, *Wear*, **225**, 146–153.

Donnet, C., Fontaine, J., Lefèbvre, F., Grill, A., Patel, V. and Jahnes, C. (1999). Solid state 13C and 1H nuclear magnetic resonance investigations of hydrogenated amorphous carbon, *J Appl Phys*, **85**, 3264–3270.

Dowling, D.P., Kola, P.V., Donnelly, K., Kelly, T.C., Brumitt, K., Lloyd, L. *et al.* (1997). Evaluation of diamond-like carbon-coated orthopaedic implants, *Diam Relat Mater*, **6**, 390–393.

Erdemir, A. and Donnet, C. (2006). Tribology of diamond-like carbon films: recent progress and future prospects, *J Phys Appl Phys*, **39**, R311–R327.

Fisher, J., Hu, X.Q., Stewart, T.D., Williams, S., Tipper, J.L., Ingham, E. *et al.* (2004). Wear of surface engineered metal-on-metal hip prostheses, *J Mater Sci Mater M*, **15**, 225–235.

Gilmore, R. and Hauert, R. (2001). Control of the tribological moisture sensitivity of diamond-like carbon films by alloying with F, Ti or Si, *Thin Solid Films*, **398**, 199–204.

Hasebe, T., Shimada, A., Suzuki, T., Matsuoka, Y., Saito, T., Yohena, S. *et al.* (2006). Fluorinated diamond-like carbon as antithrombogenic coating for blood-contacting devices, *J Biomed Mater Res*, **76A**, 86–94.

Hasebe, T., Yohena, S., Kamijo, A., Okazaki, Y., Hotta, A., Takahashi, K. *et al.* (2007). Fluorine doping into diamond-like carbon coatings inhibits protein adsorption and platelet activation, *J Biomed Mater Res*, **83A**, 1192–1199.

Hauert, R., Thorwarth, K. and Thorwarth, G. (2013). An overview on diamond-like carbon coatings in medical applications, *Surf Coat Tech*, **233**, 119–130.

Hauert, R., Falub, C.V., Thorwarth, G., Thorwarth, K., Affolter, C., Stiefel, M. *et al.* (2012a). Retrospective lifetime estimation of failed and explanted diamond-like carbon coated hip joint balls, *Acta Biomater*, **8**, 3170–3176.

Hauert, R., Thorwarth, G., Muller, U., Stiefel, M., Falub, C.V., Thorwarth, K. *et al.* (2012b). Analysis of the *in-vivo* failure of the adhesive interlayer for a DLC coated articulating metatarsophalangeal joint, *Diam Relat Mater*, **25**, 34–39.

He, X., Li, W. and Li, H. (1994). Bonding structure and tribological properties of DLC films synthesized by dual ion beam sputtering, *Vacuum*, **45**, 977–980.

Jones, B.J., Mahendran, A., Anson, A.W., Reynolds, A.J., Bulpett, R. and Franks, J. (2010). Diamond-like carbon coating of alternative metal alloys for medical and surgical applications, *Diam Relat Mater*, **19**, 685–689.

Kim, H.G., Ahn, S.H., Kim, J.G., Park, S.J. and Lee, K.R. (2005). Effect of Si-incorporation on wear-corrosion properties of diamond-like carbon films, *Thin Solid Films*, **482**, 299–304.

Kim, H.G., Ahn, S.H., Kim, J.G., Park, S.J. and Lee, K.R. (2005). Corrosion performance of diamond-like carbon (DLC)-coated Ti alloy in the simulated body fluid environment, *Diam Relat Mater*, **14**, 35–41.

Kim, J.G., Lee, K.R. and Yang, S.J. (2008). Wear-corrosion performance of Si-DLC coatings on Ti-$_6$Al-$_4$V substrate, *J Biomed Mater Res*, **86A**, 41–47.

Kwok, S.C.H., Wang, J. and Chu, P.K. (2005). Surface energy, wettability, and blood compatibility phosphorus doped diamond-like carbon films, *Diam Relat Mater*, **14**, 78–85.

Kwok, S.C.H., Zhang, W., Wan, G.J., McKenzie, D.R., Bilek, M.M.M. and Chu, P.K. (2007). Hemocompatibility and anti-bacterial properties of silver doped diamond-like carbon prepared by pulsed filtered cathodic vacuum arc deposition, *Diam Relat Mater*, **16**, 1353–1360.

Lappalainen, R., Heinonen, H., Anttila, A. and Santavirta, S. (1998). Some relevant issues related to the use of amorphous diamond coatings for medical applications, *Diam Relat Mater*, **7**, 482–485.

Lappalainen, R., Selenius, M., Anttila, A., Konttinen, Y.T. and Santavirta, S.S. (2003). Reduction of wear in total hip replacement prostheses by amorphous diamond coatings, *J Biomed Mater Res B Appl Biomater*, **66**, 410–413.

Lee, C.S., Lee, K.R., Eun, K.Y., Yoon, K.H. and Han, J.H. (2002). Structure and properties of Si incorporated tetrahedral amorphous carbon films prepared by hybrid filtered vacuum arc process, *Diam Relat Mater*, **11**, 198–203.

Lee, K.R., Baik, Y.J., Eun, K.Y. and Han, S. (1994). Precursor gas effect on the structure and properties of diamond-like carbon-films, *Diam Relat Mater*, **3**, 1230–1234.

Lee, K.R., Kim, M.G., Cho, S.J., Eun, K.Y. and Seong, T.Y. (1997). Structural dependence of mechanical properties of Si incorporated diamond-like carbon films deposited by RF plasma-assisted chemical vapour deposition, *Thin Solid Films*, **308**, 263–267.

Leu, M.S., Chen, S.Y., Chang, J.J., Chao, L.G. and Lin, W. (2004). Diamond-like coatings prepared by the filtered cathodic arc technique for minting application, *Surf Coat Tech*, **177**, 566–572.

Maguire, P.D., McLaughlin, J.A., Okpalugo, T.I.T., Lemoine, P., Papakonstantinou, P., McAdams, E.T. *et al.* (2005). Mechanical stability, corrosion performance and bioresponse of amorphous diamond-like carbon for medical stents and guidewires, *Diam Relat Mater*, **14**, 1277–1288.

McKenzie, D.R. (1996). Tetrahedral bonding in amorphous carbon, *Rep Progr Phys*, **59**, 1611–1664.

Mohanty, M., Anilkumar, T.V., Mohanan, P.V., Muraleedharan, C.V., Bhuvaneshwar, G.S., Derangere, F. *et al.* (2002). Long term tissue response to titanium coated with diamond like carbon, *Biomol Eng*, **19**, 125–128.

Ogwu, A.A., Okpalugo, T.I.T., Ali, N., Maguire, R.D. and McLaughlin, J.A.D. (2008). Endothelial cell growth on silicon modified hydrogenated amorphous carbon thin films, *J Biomed Mater Res B Appl Biomater*, **85**, 105–113.

Okpalugo, T.I.T., Ogwu, A.A., Maguire, P.D. and McLaughlin, J.A.D. (2004). Platelet adhesion on silicon modified hydrogenated amorphous carbon films, *Biomaterials*, **25**, 239–245.

Okpalugo, T.I.T., Ogwu, A.A., Okpalugo, A.C., McCullough, R.W. and Ahmed, W. (2008). The human micro-vascular enclothelial cells in vitro interaction with atomic-nitrogen-doped diamond-like carbon thin films, *J Biomed Mater Res B Appl Biomater*, **85**, 188–195.

Oñate, J.I., Comin, M., Braceras, I., Garcia, A., Viviente, J.L., Brizuela, M. *et al.* (2001). Wear reduction effect on ultra-high-molecular-weight polyethylene by application of hard coatings and ion implantation on cobalt chromium alloy, as measured in a knee wear simulation machine, *Surf Coat Tech*, **142**, 1056–1062.

Ouyang, J.H. and Sasaki, S. (2005). Friction and wear characteristics of a Ti-containing diamond-like carbon coating with an SRV tester at high contact load and elevated temperature, *Surf Coat Tech*, **195**, 234–244.

Pandiyaraj, K.N., Heeg, J., Lampka, A., Junge, F., Barfels, T., Wienecke, M. *et al.* (2012). *In vitro* cyto and blood compatibility of titanium containing

diamond-like carbon prepared by hybrid sputtering method, *Plasma Sci Tech*, **14**, 829.

Papakonstantinou, P., Zhao, J.F., Lemoine, P., McAdams, E.T. and McLaughlin, J.A. (2002). The effects of Si incorporation on the electrochemical and nanomechanical properties of DLC thin films, *Diam Relat Mater*, **11**, 1074–1080.

Platon, F., Fournier, P. and Rouxel, S. (2001). Tribological behaviour of DLC coatings compared to different materials used in hip joint prostheses, *Wear*, **250**, 227–236.

Robertson, J. (1992). Properties of diamond-like carbon, *Surf Coat Tech*, **50**, 185–203.

Robertson, J. (2002). Diamond-like amorphous carbon, *Mater Sci Eng R Rep*, **37**, 129–281.

Saikko, V., Ahlroos, T., Calonius, O. and Keränen, J. (2001). Wear simulation of total hip prostheses with polyethylene against CoCr, alumina and diamond-like carbon, *Biomaterials*, **22**, 1507–1514.

Saito, T., Hasebe, T., Yohena, S., Matsuoka, Y., Kamijo, A., Takahashi, K. *et al.* (2005). Antithrombogenicity of fluorinated diamond-like carbon films, *Diam Relat Mater*, **14**, 1116–1119.

Sánchez, N.A., Rincón, C., Zambrano, G., Galindo, H. and Prieto, P. (2000). Characterization of diamond-like carbon (DLC) thin films prepared by r.f. magnetron sputtering, *Thin Solid Films*, **373**, 247–250.

Sheeja, D., Tay, B.K. and Nung, L.N. (2005). Tribological characterization of surface modified UHMWPE against DLC-coated Co-Cr-Mo, *Surf Coat Tech*, **190**, 231–237.

Sheeja, D., Tay, B.K., Lau, S.P. and Nung, L.N. (2001). Tribological characterisation of diamond-like carbon coatings on Co-Cr-Mo alloy for orthopaedic applications, *Surf Coat Tech*, **146**, 410–416.

Shi, B., Ajayi, O.O., Fenske, G., Erdemir, A. and Liang, H. (2003). Tribological performance of some alternative bearing materials for artificial joints, *Wear*, **255**, 1015–1021.

Shim, K.S., Kim, S.M., Bac, S.H., Lee, S.Y., Jung, H.S. and Park, H.H. (2000). Fabrication and characterization of diamond-like carbon thin films by pulsed laser deposition, *Appl Surf Sci*, **154**, 482–484.

Sui, J.H., Cai, W. and Zhao, L.C. (2006). Surface modification of NiTi alloys using diamond-like carbon (DLC) fabricated by plasma immersion ion implantation and deposition (PIIID), *Nucl Instrum Meth B*, **248**, 67–70.

Thorwarth, G., Falub, C.V., Muller, U., Weisse, B., Voisard, C., Tobler, M. *et al.* (2010). Tribological behavior of DLC-coated articulating joint implants, *Acta Biomater*, **6**, 2335–2341.

Tiainen, V.M. (2001). Amorphous carbon as a bio-mechanical coating — mechanical properties and biological applications, *Diam Relat Mater*, **10**, 153–160.

Xu, T. and Pruitt, L. (1999). Diamond-like carbon coatings for orthopaedic applications: an evaluation of tribological performance, *J Mater Sci Mater Med*, **10**, 83–90.

Yokota, T., Terai, T., Kobayashi, T., Meguro, T. and Iwaki, M. (2007). Cell adhesion to nitrogen-doped DLCs fabricated by plasma-based ion implantation and deposition method using toluene gas, *Surf Coat Tech*, **201**, 8048–8051.

Zou, Y.S., Wang, W., Song, G.H., Du, H., Gong, J., Huang, R.F. *et al.* (2004). Influence of the gas atmosphere on the microstructure and mechanical properties of diamond-like carbon films by arc ion plating, *Mater Lett*, **58**, 3271–3275.