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Deposition, characterization, and tributional applications of near-frictionless carbon films on glass and ceramic substrates

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Abstract

As an element, carbon is rather unique and offers a range of rare opportunities for the design and fabrication of zero-, one-, two-, and three-dimensional nanostructured novel materials and coatings such as fullerenes, nanotubes, thin films, and free-standing nano-to-macroscale structures. Among these, carbon-based two-dimensional thin films (such as diamond and diamond-like carbon (DLC)) have attracted an overwhelming interest in recent years, mainly because of their exceptional physical, chemical, mechanical, electrical, and tribological properties. In particular, certain DLC films were found to provide extremely low friction and wear coefficients to sliding metallic and ceramic surfaces. Since the early 1990s, carbon has been used at Argonne National Laboratory to synthesize a class of novel DLC films that now provide friction and wear coefficients as low as 0.001 and 10^{-11}–10^{-10} mm^3 N^{-1} m^{-1}, respectively, when tested in inert or vacuum test environments. Over the years, we have optimized these films and applied them successfully to all kinds of metallic and ceramic substrates and evaluated their friction and wear properties under a wide range of sliding conditions. In this paper, we will provide details of our recent work on the deposition, characterization, and tribological applications of near-frictionless carbon films on glass and ceramic substrates. We will also provide chemical and structural information about these films and describe the fundamental tribological mechanisms that control their unusual friction and wear behaviour.

(Some figures in this article are in colour only in the electronic version)

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1. Introduction

Elemental carbon is the key constituent of a wide variety of engineering materials such as diamond, diamond-like carbon (DLC), metal carbides, carbon nitride, fullerenes, nanotubes, etc, which are well known for their unusual mechanical, electrical, and tribological properties. Among others, thin-film coatings of diamond and DLC have attracted particular attention during the past two decades and both have been optimized to provide much-needed performance improvements in a wide range of applications, including microelectronics, manufacturing, transportation, and rotating machinery [1, 2]. Specifically, certain DLC films were shown to provide extremely low friction and wear coefficients under dry sliding conditions in vacuum or inert gases [3, 4]. When compared to diamond, these films are much easier and less expensive to produce and use in various applications, including engine components, magnetic recording media, machining and manufacturing tools, and invasive and implantable medical devices [1, 5].

The unique lubrication mechanisms of diamond and DLC films are thought to be interrelated, and are primarily attributed to the very inert nature of their sliding contact surfaces [1, 2, 6–9]. Specifically, it has been postulated that active chemical species (such as hydrogen, oxygen, and water molecules) in the test environment can easily attach to and passivate the dangling σ bonds of carbon atoms on the surface of diamond and DLC films. Apparently, when such bonds are completely passivated, the adhesion component of friction is drastically reduced [3, 9]. Conversely, if these bonds are reactivated by ion-beam etching or thermal desorption of chemical species from the surface, their friction coefficients increase dramatically, presumably because reactivated σ bonds are free to participate in strong adhesive interactions across the sliding contact interfaces and hence cause very high friction [10, 11].

In recent years, ceramic-based materials have gained considerable popularity for various engineering applications (mainly because of their light weight; superior resistance to corrosion, oxidation, and wear; and excellent mechanical strength and hardness, even at high temperatures). At present, they are the preferred choice for mechanical pump seals that are used in all kinds of rotating machinery, including water-pump seals of diesel engines. Several other engine components (such as cylinders, pistons, valves, turbo-chargers, roller followers, fuel injectors, etc) are now fabricated from ceramics and used to enhance the performance and durability of race car and other specialty engines [12, 13]. A collection of such components, fabricated from ceramics, is shown in figure 1. These components are often subjected to a combination of rolling, sliding, or rotating-type motions in engines where abrasive wear and fatigue are the major degradation mechanisms. If not controlled or minimized, motions of this type can trigger microcracks and hence cause premature failure of the ceramic-based engine components. By virtue of their high chemical inertness, most ceramics are very difficult to lubricate by conventional oils and/or greases. Specifically, they do not respond well to the additives in these oils; hence the use of self-lubricating coatings may be necessary to achieve acceptable levels of lubricity on their sliding surfaces [14, 15].

Besides engine and pump-seal applications, ceramics are also used in the fabrication of artificial implants. Specifically, some of the femoral heads and acetabular cups used in total hip arthroplasty are now fabricated from alumina and zirconia ceramics to achieve lower friction, longer wear life, and improved biocompatibility [16, 17]. Figure 2 shows some acetabular heads and cups that have been fabricated from alumina and zirconia ceramics. At present, most of the cups are still fabricated from ultrahigh-molecular-weight polyethylene (UHMWPE).

One of the major problems in artificial implants is related to the high wear of UHMWPE regardless of the type of ceramic or metallic heads that are used. Over the years, generation and accumulation of wear debris in and around artificial hip and knee joints lead to osteolysis or

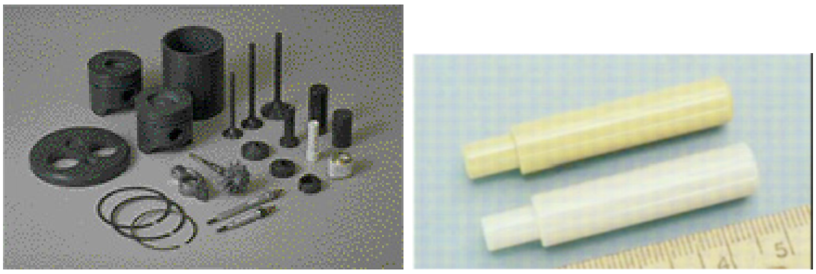

Figure 1. (a) Engine components fabricated from advanced ceramics (Kyocera Co., Fine Ceramics Division) and (b) fuel injectors fabricated from yttria- and magnesia-stabilized magnesia ceramics.

Figure 2. Implantable ceramic femoral heads and acetabular cups.

bone disintegration and hence loosening and failure of these joints. Cross-linking of UHMWPE retards the wear process considerably, but some wear particles are still generated at the contact interface of cups and heads [18]. Application of a very thin DLC film over ceramic heads appears to be an attractive possibility to control the wear of UHMWPE. These coatings may also improve the biocompatibility of the joints, because carbon is rather benign and known to be biocompatible. Recent tribological studies in bovine serum in our laboratory have confirmed that such films are, indeed, effective in reducing friction and wear of both the metallic and ceramic-based implant materials [19].

Glasses are rarely considered for tribological applications; however, some special glasses are now used as windows in laser bar code scanners and other optical systems where high wear resistance, in addition to high transparency, may be critically important. Rubbing or scrubbing of hard objects over these glasses may cause abrasive wear, which can, in the long term, impair their transparency and hence their performance. Therefore, application of a thin DLC film on such glasses may increase their resistance to scratching while preserving transparency. Certain types of glasses are also used in the fabrication of various planar microarrays and microchannels that have increasingly become integral parts of digital microfluidic and micro-electro-mechanical system devices [20]. Thin DLC films can also be applied to control the stiction, adhesion, and hydrophobic-versus-hydrophilic behaviour of such devices.

DLC has been investigated as a coating for a secure fingerprint module. The device contains a prism made of glass, polycarbonate or acrylic, which is vulnerable to scratching. The process of coating glass or polycarbonate is reasonably straightforward and, when the coating is thin enough, the optical properties of the prism are not compromised. The acrylic was more challenging because it is a softer material and exhibits a low melting point. However, it was found that etching the material with oxygen could functionalize the surface and make it amenable to the adhesion of DLC. The coating must be able to take a fingerprint, even from dry skin, as well as improve hardness.

It is obvious from the foregoing that many glass and ceramic-based tribological components can benefit from the application of thin DLC films on their sliding surfaces. Accordingly, in this paper, we will concentrate mainly on the friction and wear behaviour of DLC-coated glass and ceramic materials. We will focus our attention on the synthesis and characterization of a superlow-friction carbon film (which we call near-frictionless carbon, or NFC) that can significantly enhance the friction and wear performance of glass and ceramic substrates. The specific deposition conditions that are necessary for the synthesis of these NFC films are also provided, as are details of their chemical composition and structure. A fundamental mechanism is proposed to explain the superlow friction and wear properties of these NFC films when applied on glass and ceramic substrates.

2. Experimental procedures

2.1. Test materials

In this study, in addition to several pieces of tempered window glass we have obtained and used several ceramic substrates, including alumina, yttria-stabilized zirconia, sapphire, and SiC. Spherical balls and flat squares or discs of these glass and ceramic materials, with and without an NFC film on their sliding surfaces, were used in our friction and wear experiments. We also applied NFC films on the rotating faces of SiC seals that are used in mechanical pumps. The surface finish of all of these substrates was mirror-like, with an RMS surface roughness $< 0.01\ \mu$m. The range of substrates used in this study is representative of advanced ceramic materials that are currently being used in various tribological applications. Among the evaluated substrate materials, glass and zirconia are relatively soft and less rigid than alumina and sapphire. Specifically, the hardness values of glass and zirconia are respectively $\approx$8 and 12 GPa on the Vickers scale, whereas Vickers hardness values of alumina and sapphire are respectively $\approx$17 and 35 GPa. When subjected to concentrated sliding contact situations in a pin-on-disc machine, the extent of Hertzian contact pressures (both peak and mean pressures) created on glass and zirconia is expected to be much lower than those created on alumina and sapphire substrates. Hence, the results of the pin-on-disc experiments may reveal if contact pressure depends on friction.

2.2. Deposition of NFC

To deposit NFC films on glass, alumina, zirconia, and sapphire substrates, we used a plasma-enhanced chemical vapour deposition (PECVD) system (Perkin-Elmer model 2400). These films were synthesized in a gas discharge plasma that consisted of 25 vol% methane (CH_4) + 75 vol% hydrogen (H_2). The procedure for forming the NFC films on ceramic and glass substrates involved several important steps. First, before loading the materials into the deposition chamber, they were solvent cleaned in an ultrasonic bath of acetone and methanol to remove organic contaminants from their surfaces. They were then loaded into the deposition chamber, where they were subjected to a sputter-cleaning step by creating and using an Ar plasma for 30 min. The rf bias applied to the substrates during this cleaning process was $\approx$500 V_{DC}. During the sputter-cleaning step, most of the chemically bound contaminants were removed from the surface. Such atomically clean surfaces can attain very strong bonding or adhesion to the intermediate bond layers that are to be deposited on the surface. The third step was the deposition of an intermediate 50–70 nm thick Si bond layer. The Si bond layer was produced on the atomically cleaned surfaces of glass and ceramic substrates by switching the PECVD system from sputter-cleaning mode to sputter-deposition mode. For this step, we could either sputter silicon from a target or use silane (SiH_4) gas. In both cases, we could produce a strongly bonded Si intermediate layer that can provide strong bonding not only to the glass and ceramic substrates but also to the NFC films that were deposited as the last step. The appropriate CH_4–H_2 mixtures were established and introduced into the deposition chamber and the deposition of DLC on the substrates was initiated. The total gas pressure in the deposition chamber varied between 10 and 13 mTorr and the rf bias was at 500 V_{DC}. The nominal thickness of the NFC films produced on ceramic substrates was $\approx 1\ \mu$m. The films produced on glass substrates were much thinner, i.e., 50–100 nm thick. Further details of the deposition process can be found in [3] and [21].

2.3. *Friction and wear tests*

The coated samples were tested for their friction and wear performance with a ball-on-disc tribometer and a reciprocating test machine. In all of these tests, we used coated glass, alumina, sapphire, and zirconia ceramics as test samples. Pin-on-disc tests were performed in a dry nitrogen environment under a 5 N load to determine the friction and wear performance of NFC under inert test conditions. The sliding velocity was 0.3 m s^{-1} and the sliding distance was up to 5 km. To measure the friction coefficient of the DLC coating against itself, both the ceramic balls and the discs were coated with DLC. Each pair was tested two to three times to check the repeatability of the test results. The test chamber was purged with dry nitrogen for at least 30 min after 0% humidity was shown on a hygrometer display unit. Wear volume (W_b) of the balls was determined with an optical microscope; the diameter of the wear scar and ball were inserted in the equation $W_b = 3.14d^4/64r$, where r is the ball radius, d is the diameter of the wear scar, and W_b is the wear volume. To simplify the calculation, we assumed that the wear scar was flat; a three-dimensional optical profilometer confirmed the formation of very small flat wear scars on ball sides.

2.4. *Seal tests*

The uncoated and NFC-coated SiC seals (rotors) were tested in a seal test machine. They were mounted on the opposite ends of a steel shaft that passed through a water-filled test chamber. The rotors were pressed against the uncoated SiC seal rings (stators). For testing purposes, the test chamber can be pressurized, up to 400 psi (2.8 MPa), by passing compressed air through air cylinders that are attached to the test chamber via stainless steel tubes. The seal test machine featured water level and temperature monitors to provide feedback signals for system shutdown in case of leakage or water level reduction below the minimum required for safe operation. This shut-off capability avoids seal damage that would occur under dry running conditions. The water temperature provides a means to monitor the frictional behaviour of the seals. In the present case, all of the tests were carried out in water at 200 psi ($\approx$0.7 MPa) chamber pressure with an axis rotational speed of $\approx$3600 rpm. These test parameters represent typical operating conditions for pumps used in several industrial applications. The total test time was 200 h. The chemical nature of these NFC films was characterized by Raman and x-ray photoelectron spectroscopy methods. Optical noncontact profilometry and scanning electron microscopy were used to determine the wear and surface morphology of the tested samples.

2.5. *Friction and wear tests in bovine serum*

Friction and wear tests were conducted in a reciprocating test rig using ‘pin’ samples made of 1.27 mm diameter zirconia and alumina balls; the flat samples were made of polished 440C

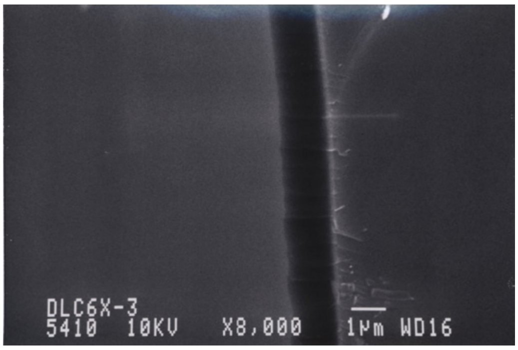

Figure 3. Typical SEM cross-sectional image of NFC film deposited on Si substrate.

stainless steel. All of the samples and their holders were well cleaned and sterilized before the tests. The friction coefficient was determined from the friction force measured by a load cell attached to the pin assembly. The friction coefficient was continuously monitored and recorded during each test. Tests were conducted at the normal load of 50 N and frequency of 1 Hz, which translate to an average relative surface velocity of 50 mm s^{-1} for a 25 mm stroke length. Commercial bovine blood serum was used as the lubricant. The test pairs were submerged in a cup that held the lubricant during testing. The duration of each test was 1 h. The four evaluated pin materials were a stainless steel ball, Al_2O_3, ZrO_2, and NFC coating.

3. Results and discussion

Figure 3 shows the typical cross-sectional morphology of an NFC film used in this study. As can be seen, the microstructure of the film is essentially featureless, with a nominal thickness of $\approx$1 μm. The surface roughness of the films was in the nanometre range and mimicked the surface contours of underlying substrates. Earlier nanomechanical tests have shown that these films had average hardness and elastic modulus values of $\approx$14 and $\approx$60 GPa, respectively [21]. Near-edge x-ray absorption fine structure studies have revealed that they consisted of $\approx$70% sp^2- and 30% sp^3-bonded carbon atoms. A forward-recoil scattering method revealed that these films consisted of $\approx$40 at.% hydrogen [22].

3.1. Friction and wear of NFC-coated ceramic and glass substrates

The variation of the friction coefficients of NFC-coated sapphire and alumina test pairs during sliding in dry N_2 is shown in figure 4. The friction coefficient of the NFC-coated sapphire pair is initially $\approx$0.05 but it decreases rapidly during consecutive sliding cycles and reaches a value of $\approx$0.001. It is important to remember that the steady-state friction coefficient of an uncoated sapphire ball against an uncoated sapphire disc was $\approx$0.9 in dry N_2, when tested under the same conditions. Initially the friction coefficient of NFC-coated alumina test pairs is $>$0.1, but after $\approx$2000 s it reaches a value as low as 0.002. Several scientific reasons could account for such a disparity in the frictional behaviours of these two substrates. Chemically their composition is the same, but mechanically sapphire is much harder and more rigid than alumina. Another key difference is the roughness; while the nominal RMS surface finish of sapphire is $>$1 nm, that of alumina is $\approx$10 nm. It is well known that the physical roughness of a sliding surfaces adversely affects friction and wear behaviour. In general, the higher the surface roughness, the higher the friction coefficients. Hence, the very high initial or break-in friction coefficient of the

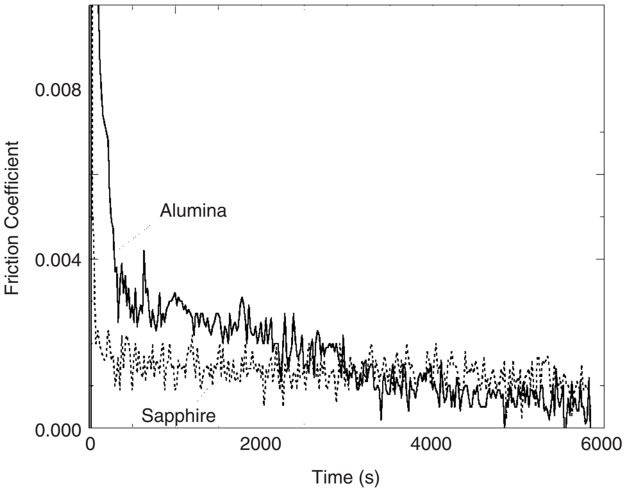

Figure 4. Variation of friction coefficients of NFC-coated alumina and sapphire test pairs with sliding distance.

NFC-coated alumina substrate may have been largely due to its rougher surface finish. During the course of repeated sliding passes, the contact interface between the NFC-coated alumina ball and disc becomes smoother, and hence the friction coefficient comes down to the much lower steady-state values shown in figure 4. Large differences in the mechanical properties of these substrates may have contributed to the observed disparity in the frictional behaviour of sapphire and alumina; more-rigid and hard sapphire can provide better support for the NFC film and achieve a smaller contact area, which leads to lower friction.

The wear of NFC-coated alumina and sapphire substrates was difficult to measure after the 5 km long sliding tests. A small wear scar appeared to have formed on the sides of the balls, but the assessment of their wear rate (which would have required the formation of a flat wear scar) was difficult. Some wear particles could be detected around the rims of contact spots, but after they were wiped off with a soft tissue, there was no clear evidence of a flat wear scar on these spots.

Figure 5(a) shows the frictional behaviour of an NFC coating produced on a glass substrate. The counterface alumina ball used in this experiment was also coated with NFC (about 100 nm thick). As is obvious, the friction coefficient of this pair starts high, but decreases very rapidly, and, after a sliding distance of $\approx$20 m, it reaches a value of 0.02. Note that this is a much higher friction coefficient than that obtained on NFC-coated sapphire or alumina test pairs. The higher friction coefficient of NFC on glass could be due to two factors: the glass substrate here is softer than both alumina and sapphire, and the thickness of the films produced on glass substrates is 10 times thinner. These thinner films are rather transparent, even at a thickness of 100 nm, see figure 5(b).

Evidence of wear on these sliding surfaces is shown in figure 5(c); specifically, wear debris was produced during the sliding action and accumulated around the edges of wear scars and tracks. Again, such high levels of wear of NFC-coated glass substrates may have been due to the softness of the base glass, smaller film thickness, and, perhaps, relatively poor adhesion. In this preliminary study, we did not attempt to optimize film adhesion and thickness with respect to tribological properties; the main objective was to demonstrate that very thin NFC films could be deposited on glasses without significantly impairing their transparency.

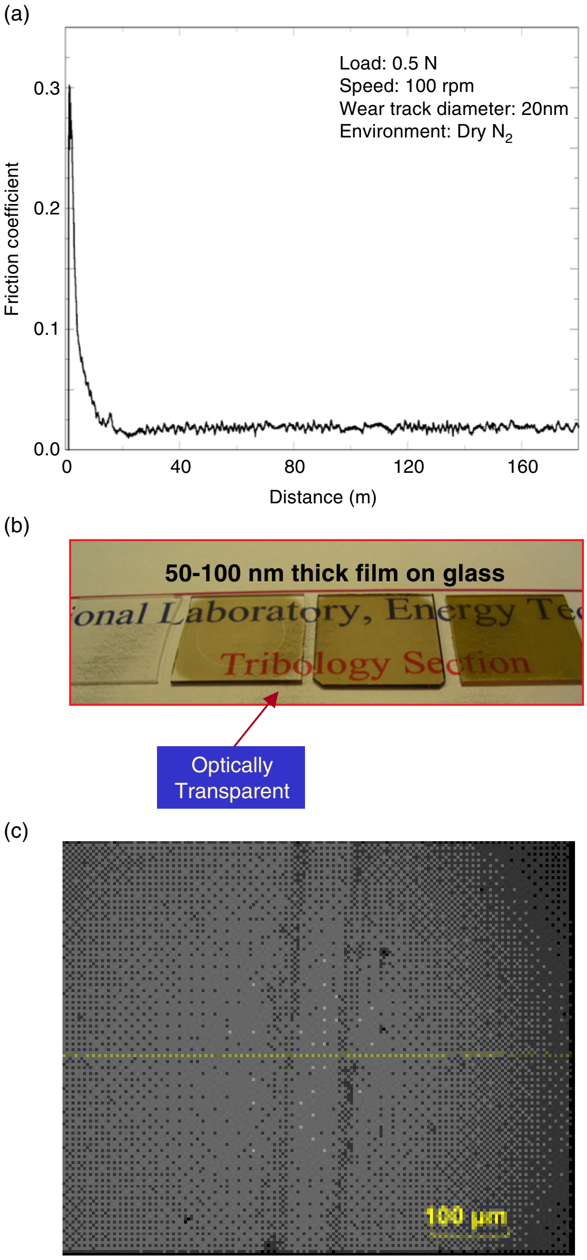

Figure 5. (a) Variation of friction coefficient of NFC-coated alumina balls during sliding against a glass substrate; (b) illustration of transparency; (c) wear scar wear of sliding alumina pin on glass disc contact surface.

3.2. *Friction and wear of NFC-coated test pairs in bovine serum*

The average friction coefficients of various test pairs in bovine serum are shown in figure 6. From the figure we see that the average friction coefficient of uncoated ceramics sliding against uncoated 440C steel discs was ≈0.1, whereas that of NFC-coated pairs was ≈0.05, representing

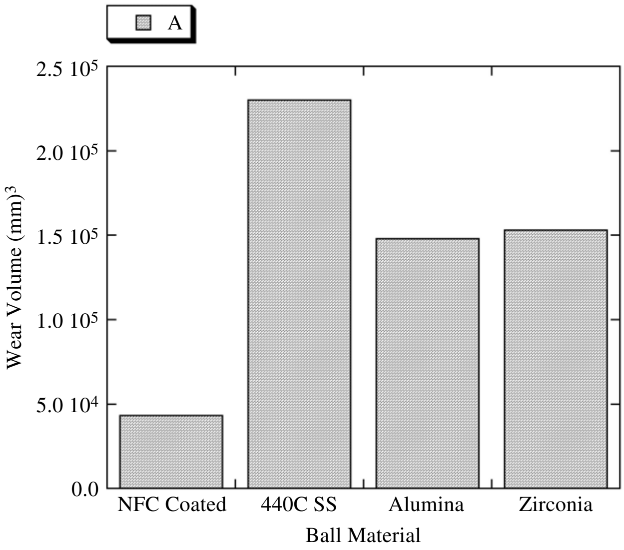

Figure 6. Friction coefficients and wear volumes of various test pins slid against 440C stainless steel in bovine serum.

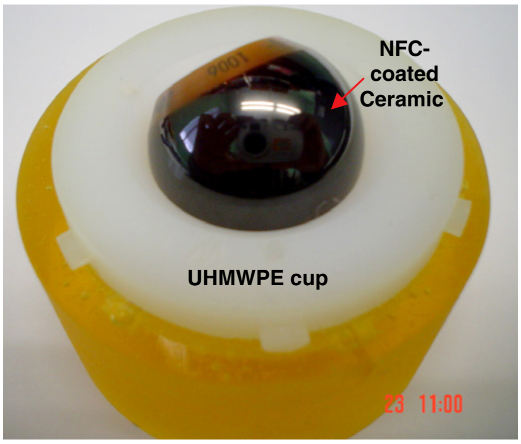

Figure 7. NFC-coated zirconia ceramic head with UHMWPE cup.

a significant reduction, especially because Al_2O_3 and ZrO_2 are currently being used as implant materials. Similarly, an order of magnitude reduction in wear was observed for cases where NFC coatings were used in comparison with uncoated alumina and zirconia ceramic materials as shown by the values of the bar graph in figure 6. In view of the fact that wear and the consequent occurrence of osteolysis are the prime issues in artificial joint implants, an order of magnitude reduction in wear is expected to translate into much increased durability of these products. Figure 7 shows a ceramic head coated with NFC film.

Figure 8. General view of NFC-coated (left) and uncoated SiC seal after 200 h tests.

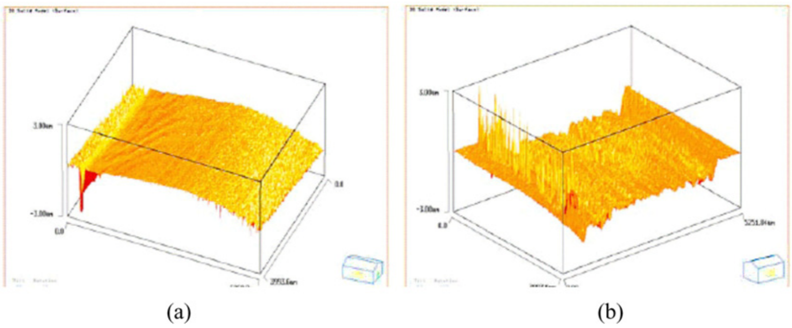
(a) (b)

Figure 9. 3D surface images of (a) NFC-coated and (b) uncoated SiC seal faces after tests under 200 psi pressure and 3500 rpm rotational speed for 200 h.

3.3. Friction and wear performance of NFC-coated SiC seals

General images of uncoated and NFC-coated SiC seal faces after testing for 200 h under a 200 psi face pressure are shown in figure 8. Figure 9 shows high-resolution 3D images of these seal faces, as generated by an optical non-contact profilometer. Figure 9(b) clearly shows that significant wear had occurred on the uncoated SiC seal face, while very little wear had occurred on the NFC-coated SiC seal face, as shown by the left-hand image of figure 8. The deep wear groove observed near the inner edge of the NFC-coated seal is most likely due to the high stress concentration on this area. In general, there is a significant stress gradient from the inner to the outer edges of seals during operation and the high levels of stress on or near the inner edges always cause higher wear in these areas; this can also be noticed on the uncoated seal face in figure 9(b). During the 200 h test, we did not notice any leakage from the NFC-coated seal face, whereas some water had leaked out of the uncoated seal face.

We provide the following explanation for the excellent wear resistance of NFC-coated seal faces. Because of its low friction nature, we believe that NFC was better able to keep rotating seal faces cool; hence it could reduce or eliminate the sources of thermomechanical and tribochemical wear. The low friction of NFC-coated seal faces also ensures that the magnitude of orthogonal shear forces is small and that they are shifted well below the sliding surfaces. This, the probability of crack initiation on these surfaces is highly unlikely. In short, the seal test results of this study clearly demonstrate that NFC films hold high promise for demanding seal applications, and suggest that these films may eliminate leakage of hazardous chemicals to the environment by providing better seals during operation.

3.4. *Friction and wear mechanisms of NFC films*

The main characteristics of NFC films used in this study are determined by the fact that they were synthesized in a gas discharge plasma that consisted of 75% H_2 and 25% CH_4. This means that there were ten hydrogen atoms per carbon atom in the plasma. We believe that the excellent friction and wear behaviour of films grown in such plasmas is closely associated with the fact that they are superhydrogenated. As mentioned earlier, in most carbon-based films hydrogen plays perhaps the most important role in their frictional performance [3–11]. Hydrogen has a high capacity to bond strongly with and passivate dangling σ bonds, thus creating surfaces that are inert to objects that may be in static or sliding contact with them. We believe that, in NFC films, almost all of the dangling σ bonds were passivated by hydrogen.

Briefly, we believe that hydrogen plays an important role in the friction and wear behaviour of all carbon films. Carbon films grown in hydrogen-rich gas discharge plasmas (like NFC) provide very low friction coefficients, mainly because their surfaces are chemically passive, and hence do not enter into strong bonding or chemical interactions during sliding contact.

4. Conclusions

From the friction and wear test data presented above, it is clear that thin NFC films produced on glass and ceramic substrates can have a huge positive impact on the friction and wear properties of these substrates. Specifically, when applied on glass, alumina, and sapphire surfaces, these films can lower friction to the 0.001 level but the amount of wear is difficult to quantify. Such impressive behaviour could be due to the high chemical inertness of these films. When applied on SiC pump seals, these films can provide excellent protection against wear and hence hold promise for applications that involve rotating contacts. NFC films can also lower friction and wear of sliding ceramic surfaces in bovine serum. They can be produced on surfaces of ceramic femoral heads and may have significant beneficial effects on the friction and wear of such components.

Acknowledgments

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