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Tribological Behavior of Duplex Nitrogen Diffusion/Dlc Coating Treatments.

Yan Liu
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TRIBOLOGICAL BEHAVIOR OF DUPLEX NITROGEN DIFFUSION/DLC COATING TREATMENTS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy in

The Interdepartmental Program in Engineering Science

by

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Diamond-like carbon (DLC) coatings have high potential for developing advanced tribological systems and the overall objective of the present research is to provide a framework to theoretically design and experimentally develop and study such systems of interest. The present research concentrates on the following specific aspects: the fundamental wear mechanism of DLC coatings; finite element (FE) modeling to understand the stress distribution in coating/substrate system under indentation and friction; and the influence of graded interface on the tribological behavior of DLC coatings.

The experimental results showed that DLC films possess low friction coefficient ($f_{min}: 0.12-0.20$, $f_{fin: 0.06-0.08}$) and low wear rate ($1.6 \times 10^{-9} \text{mm}^3 \text{m}^{-1} \text{N}^{-1}$). The friction behavior of DLC coatings includes three distinct regimes: a break-in period, an intermediate constant friction plateau and a steady-state stage. The intermediate plateau coincides with the formation of a carbon-rich transfer layer on the counter-surface, and the steady-state stage with graphitization of the DLC structure. A wear-induced graphitization mechanism is proposed based on the experimental evidence. Operational and environmental parameters have significant effects on the friction process of DLC coatings through their influence on graphitization.

The results of FE modeling showed that coating thickness, contact stress and the ratio of coating/substrate properties affect the yielding of coating/substrate system.
The calculations also revealed that a graded interface can significantly decrease the size of the plastic zone in the substrate during indentation/friction and thus can improve coating behavior.

An innovative concept is the advanced coating systems with a functionally-graded interface (FGI). This concept was experimentally studied by developing DLC coatings with FGI based on the theoretical FE predictions. It was found that the durability of the DLC film is affected by the presence of the FGI and the loading. Under low loading, FGI has a small effect due to the limited yielding occurring in the substrate. Under high loading, the presence of FGI produced significant improvements (~80% increase in coating lifetime) by reducing the plastic zone size and preventing yielding at the coating/substrate interface, which is consistent with the FE predictions.
I. INTRODUCTION

The phenomena of friction and wear are mainly dependent on the interaction between material surfaces and the environment. Thus, surface modification techniques are widely used for the modification of tribological surfaces in order to reduce friction and wear damage of materials. Surface modification has advantages over bulk material treatments, because it allows a combination of "tailored" surface characteristics, i.e., optimized for wear resistance, with desirable bulk material properties (i.e., strength and rigidity).

The surface hardness (or the yield strength) is thought to be of prime importance in wear resistance because the wear rate is inversely proportional to the surface hardness. Thus, historically development of materials with hard surfaces has been imperative for wear protection. Over the past decade, surface modification techniques including chemical vapor deposition (CVD), physical vapor deposition (PVD), together with plasma assistance have been well established to develop widely used hard coatings of nitrides, carbides and carbonitrides. Hard coatings including TiN, Ti(C,N), Ti(B,N), (Ti,Al)N, CrC, etc., are currently used in industry on cutting tools, magnetic recording media and other wear resistance surfaces [1-4]. However, the interface issue between the "soft" metallic substrate and the hard coating remains a major problem that is unresolved. To meet new challenging applications in the future and develop advanced tribological systems, novel materials and innovative approaches in extending the durability of engineering surfaces should be considered.
The hard forms of amorphous and hydrogenated carbon, also known as diamond-like carbon (DLC), have recently aroused considerable interest as a high potential coating material. These forms of carbon are metastable, amorphous and contain both $sp^2$ and $sp^3$ hybridization structures. First deposited by Aisenberg and Chabot in 1971 [5], DLC films can now be prepared by different processes including d.c. and r.f. sputtering methods, plasma-assisted (PA) CVD, and ion-beam deposition from a variety of carbon bearing gaseous source materials [6-10]. DLC films are characterized by extreme hardness (3000-9000 kg/mm²) and high elastic modulus [11], a generally low friction coefficient and low wear rate [12,13]. The films typically have high optical transparency over a wide spectral range, high electrical resistivity and chemical inertness to both acids and alkalis [14,15]. The high hardness and chemical resistance of DLC films make them excellent candidates for advanced wear-resistant coatings on metals, ceramics, optical or electronic components [16].

Tribological properties of DLC films have been reported [17-25] and they demonstrate high wear resistance and low coefficients of friction ($f < 0.15$). Presently the proposals for the wear behavior of DLC films are under controversy and the fundamental wear mechanism is not well understood.

It should also be noted that most of these initial studies have been conducted on DLC films deposited on “hard” substrates (ceramics and hardened steels), whereas very little work has been done on the properties of DLC on “soft” substrates. Stress field analysis on sliding contacts under loading has established that when the coefficient of friction is reduced (as is the case with DLC films), significant shear stresses are developed and the location of the maximum shear stress moves gradually into the
substrate away from the surface. There is initial evidence [26] suggesting that under these conditions, soft substrate materials, i.e., annealed Ti-6Al-4V alloy, may not be able to provide adequate support for the hard DLC films, adversely affecting their tribological performance and durability.

An innovative approach in improving tribological behavior in such cases is to design and develop systems incorporating multilayers and/or duplex diffusion/coating treatments [26,27]. For instance, plasma nitriding has the potential to be used as a precursor treatment in these cases to harden the substrate and produce a functionally-graded interface (FGI). Such hardening (strengthening) can retard deformation of the subsurface layer reducing the abrupt change in strain and improving its distribution at the DLC coating/substrate interface, thus minimizing coating deflection. All of the above factors can have a profound effect on film wear behavior and their understanding is needed for the development of advanced tribological systems.
II. OBJECTIVES

Previous experimental results show that DLC films exhibit excellent wear resistance and low friction coefficients. They have great potential for a wide range of engineering applications. However, a fundamental understanding for this behavior and the issue of adhesion of DLC films on their substrates under frictional loading have not been developed yet. The investigation of the tribological behavior and wear mechanism of DLC films is the key element for the successful modification of their properties. Also, there is initial evidence suggesting that the subsurface layer of the substrate may have a fundamental impact on the tribological behavior of DLC and other hard films. Thus, the objectives of the present research are:

- to increase our scientific understanding of the wear mechanism of hard DLC films;

- to investigate the effect of substrate surface hardening on the tribological behavior of DLC films. The films will be developed on surface hardened Ti-6Al-4V alloy by utilizing plasma-assisted nitrogen diffusion treatments;

- to conduct finite element (FE) modeling in order to provide the theoretical information of yielding behavior in a system composed of a hard coating deposited on a graded interface, developed in a soft substrate.
III. REVIEW OF PRESENT UNDERSTANDING

A. Surface Modification Techniques

Surface modification techniques utilize lasers, ion and electron beams, CVD and PVD processes, etc. to improve surface-sensitive properties of materials such as wear, corrosion and fatigue crack initiation. Ion beam and plasma methods are most widely used at present for modification of surfaces. A brief description of some of these processes is given below.

1. Ion-beam and plasma methods

Ion implantation Ion implantation is an effective physical modification of a shallow surface region, normally with the depth of < 2000 Å [28]. It involves the introduction of one or more atomic species into the surface of a substrate material by using a high energy ion beam. This results in modified physical and chemical properties of the near surface layer. The solubility limits of the system may be exceeded since this is a non-equilibrium process. A key point for the improvement of mechanical properties of a material is the formation of controllable precipitates which can impede dislocation movement and increase strength of the material markedly [29]. The high expense of the apparatus for ion implantation and the line-of-sight requirement are the main disadvantages of this technique.

Ion plating Ion plating is a deposition process in which the substrate surface is coated with a film, deposited by a flux of high energy particles from an activated source and a pre-induced ionized plasma [30]. It is also possible to introduce a reactive gas into
the system to produce reactive ion plating. The coating ions not only adhere to the surface, but also at the beginning of the process are implanted into the immediate substrate surface providing a layer of intermixing between the substrate and coating. In general, conventional ion plating is conducted at a high temperature (700°C-1000°C) and relatively high pressure (1000-1300 Pa) and is characterized by a small degree of ionization [31-33]. One of the most commonly ion-plated compounds is titanium nitride. However, many other carbides, nitrides, and oxides as well as pure metal coatings have been prepared and are being studied [34-36].

**Ion-beam deposition (IBD)** IBD is a technique in which the ion beam including energetic particles is the source of atoms deposited in the film [37]. The bombardment of a growing film with energetic particles has been observed to produce beneficial modification in a number of characteristics and properties critical to the performance of thin films and coatings, such as improved adhesion, densification of films grown at low substrate temperatures, modification of residual stresses, control of texture (orientation), modification of grain size and morphology, modification of optical properties and modification of hardness and ductility. Ion beams have also been used in conjunction with other deposition processes in order to take advantage of the beneficial effects of energetic bombardment on film characteristics. These processes are referred to as ion beam-assisted deposition techniques.

**Plasma treatments and plasma-assisted deposition** Plasma treatments are used as thermal diffusion processes for the production of hard, corrosion, wear and fatigue-resistant surfaces. Plasma-assisted deposition utilizes the glow discharge to activate gas species that are needed for a particular PVD or CVD process [38].
Nitrogen, carbon, boron and other chemical elements can be added to the surfaces of steels and non-ferrous alloys by bringing an activated nitrogen-, carbon- or boron-bearing gas onto these surfaces, which are usually being held at an elevated temperature. This treating technique has some advantages over molten bath techniques: it permits better control over the final composition, structure and thus mechanical properties of treated surfaces; the electrical glow discharge permits higher deposition rates with required active species at lower surface temperatures in a low-pressure gas mixture and thus eliminates the expensive post cleaning operations as well as serious environmental problems.

Plasma nitriding is already a commercially viable process to develop superficially hard, corrosion, wear and fatigue-resistant surfaces. Recently, Intensified Plasma-Assisted Processing (IPAP) has been developed to enhance the ionization rate during nitriding, which allows processing of materials at low temperatures [39]. Plasma intensification is accomplished by a triode discharge and can be utilized for low-pressure, low-temperature diffusion treatments and synthesis of a range of advanced compounds. The energetic flux of ions and neutrals generated in IPAP can create highly favorable surface conditions producing significant improvements in properties ranging from thermal and chemical stability to wear resistance.

Also, concerning conventional treatments, plasma carburizing, although not so well developed at the present time, promises a great commercial benefit potential. Both plasma boriding and plasma titanizing, being investigated by many researchers, are expected to substitute for diffusion coatings in commercial scale.
2. Duplex treatments and multilayers

In many coating methods, an abrupt interface between the coating and substrate can lead to high interfacial stresses and poor adhesion. The mismatch in mechanical and physical properties can be reduced by introducing duplex treatments or multilayers on material surfaces. In general, the purpose of these treatments on material surfaces can be divided into three classes as follows:

**Improving the adhesion of top coating on to substrate** The first method for modification of adhesion between coating and substrate is to use, for example, plasma nitriding as a pretreatment. It has been shown that TiN coatings deposited by ion plating on tool steels can be optimized by utilizing plasma nitriding as a pretreatment to obtain an improved mechanical support for these coatings [40]. The second method is to produce a transition layer by sputtering. For example, it has been reported that before deposition of TiB₂ and Ti(B,N), a 0.5 μm intermediate layer of titanium was sputtered onto the substrate to improve the subsequent coating adhesion [41]. The third method is to develop a graded interface between the film and substrate using ion beam mixing. For example, the high value of interfacial energy of evaporated copper on sapphire substrate was lowered by ion-beam mixing with 1.5 MeV xenon. Peeling and wetting tests have demonstrated the enhancement of copper adhesion on the substrate [42].

**Formation of metastable or amorphous phases** Multilayered films such as Cu/Mo, Pb/Fe/Pb, Al/Cu/Fe and Al/Pb/Fe systems have been developed [43] by vapor-deposition and then exposed to high-power ion beam using 70% C⁺ and 30% H⁺ ions with energies of 0.2-0.5 MeV and flows of 1-2.2 J cm⁻². It was found that a metastable
phase was produced in the near-surface layers after irradiation, resulting in new properties.

Modifying the mechanical and other properties of coatings. Ion beam modification of sputtered MoS$_x$ film results in denser amorphous structure which produces a considerable improvement of the sliding life of the lubrication films [44,45]. Recently, it was reported that the tribological properties of pure aluminum surfaces were improved remarkably by the combined treatment of ion implantation and ion nitriding, compared with treatment using just one of these techniques [46,47]. Also, studies utilizing combined cyclotron resonance (ECR) plasma nitriding and ion implantation showed similar results [48].

A multilayer (ML) is an artificial material with one-dimensional periodic structure. There is currently considerable scientific and technological interest in MLs due to their unique properties [49]. Up to now, multilayers have been manufactured in order to satisfy the special purposes in chemistry, electronics, etc. [50-53]. Some applications of multilayers for mechanical purposes have been reported before [43]. An interesting study [54] involved the investigation of mechanical properties of laminated microscale composites of Al/Al$_2$O$_3$ (interlayer spacing ranging between 50 to 500 nm). It was found that this kind of composites can produce strength levels to the order of $\mu/70$, where $\mu$ is the shear strength of aluminum, with useful ductility and tear resistance. The experimental results showed that the Al/Al$_2$O$_3$ boundaries were extremely resistant to decohesion and cavitation over a range of temperatures and that the damage processes at Al/Al and Al/Al$_2$O$_3$ boundaries are markedly different. The composites retain their
strength levels despite exposure at high temperatures, and thus represent a useful approach to the development of high strength materials.

B. Tribological Behavior of Modified Surfaces

1. Fundamental wear mechanisms of materials

Figure 1 schematically illustrates the different types of interaction between a surface and its environment. According to the motion, the action can be described as sliding, rolling, oscillating, impacting and flowing. Similarly wear processes can be classified as sliding, rolling, oscillating, impacting and erosive wear, depending on the kinematics of the system. Other descriptions of wear processes include the physical state of the counter body, e.g. solid or liquid, or the angle of action. Related to the interfacial element, wear processes are called dry or lubricated, e.g. lubricated rolling wear, or 2-body and 3-body wear.

According to Jahanmir [55], four basic wear mechanisms or any combinations of them are involved in wear processes:

Adhesive wear Adhesive wear can occur when two surfaces slide against each other. High local pressure between contacting asperities results in plastic deformation, adhesion and consequently the formation of local junctions. Relative sliding between the contacting surfaces causes rupture of these junctions and frequently the transfer of material from one surface to the other. According to Archard law [56], the wear volume can be represented by:
Figure 1 Classification of wear processes.
where \( P \) is the normal load, \( x \) is the sliding distance, \( H \) is the penetration hardness of the softer material, \( K \) is the possibility for the rupture of any given junction between contacting asperities. Basically, \( K \) is determined by the relative strength of junction interface to the strength of the asperities that make up the junction. A weaker interface, compared with the asperities, results in a lower value of \( K \). Dissimilar material pairs should have lower values of \( K \) than similar or identical pairs. Lattice parameters and material solubility characteristics can both be the factors in determining the degree of similarity. The lower the surface energy of involved materials, the lower the \( K \) value. With respect to a clear metal surface, a lubricated surface tends to have lower surface energy and to have a lower \( K \) value than an unlubricated surface. In addition, adhesive wear is also influenced by the nature of asperity load, size and distribution, which can be manifested in a minimum load criterion for an adhesive wear fragment to be formed.

**Abrasive wear** Abrasive wear is the displacement of material caused by the presence of hard particles, embedded in one or both of the surfaces in relative motion, or by the presence of hard protuberances on one or both of the relatively moving surfaces. A "hard particle" may be the product of processing, e.g. a mineral such as silica, alumina or other ores, or a work-hardened wear fragment, or arise from the adventitious entry of hard particles from outside the tribosystem. Protuberances such as asperities on normally machined surfaces may act as "hard particles" if the surface is much harder than the counter surface. The general equation for wear volume in abrasion can be written as:

\[
V = \frac{KPx}{3H}
\]
where \( P, x, H \) have been defined previously and \( \alpha \) is a combined factor taking into account sharpness, probability of wear and the nature of wear process, as well as additional material properties. Two-body abrasive wear generally has higher \( \alpha \) than three-body conditions, because in the latter, the abrasive grain is free to move along the surface and may not always produce wear. The larger the abrasive grain, the larger the value of \( \alpha \). Lubrication tends to increase abrasive wear because liquid lubricants at the interface help to flush wear debris which tend to accumulate at the interface and share the load with the asperities. When the rubbing surfaces become sufficiently contaminated with debris, the effective abrasive action decreases.

**Surface fatigue** The basic concept of surface fatigue is that with repeated sliding, rolling or impacting, and the material in the vicinity of the surface experiences cyclic stress. As a result of this action, cracks (or damage) are initiated in these regions. With further cycling, the cracks propagate, eventually intersecting with the surface. This crack network then produces free particles which are easily removed from the surface by a subsequent motion, thereby resulting in material removal (wear). This wear surface also experiences stress cycling and the process continues, resulting in progressive loss of material from the surface.

The general form of the relationship (Pamgren's equation), for both point and line contact situations, between load and number of revolutions during incubation is [57]:

\[
V = \frac{\alpha Px}{H}
\]
\[ N_1 P_1^n = N_2 P_2^n, \]  

where \( N_1 \) and \( N_2 \) is the number of revolutions required for incubation under a load of \( P_1 \) and \( P_2 \), respectively. For the point situation, such as in a ball bearing, \( n \) is 3 and for a line contact, such as roller bearing, \( n \) is 10/3. A more fundamental form of this equation relates stress to number of revolutions. Since according to elastic contact theory [58], the maximum stress, \( S_m \), in a point contact situation is proportional to \( P^{1/3} \), the stress form of the above equation becomes:

\[ N_1 S_m^9 = N_2 S_m^9. \]  

The progression of wear scar morphology for fatigue wear under sliding conditions was studied in Cu [59]. Three stages were found during sliding: i) formation of grooves and striations in the direction of sliding due to local stress systems associated with individual asperity contact; ii) cross-hatching associated with the overall stress system of macro-geometry and with the initiation and growth of subsurface cracks; iii) loss of material due to spalling and flaking. It was found that the number of cycles required to initiate the third stage could be correlated to the maximum shear stress associated with the macro-geometry.

**Tribochemical reaction** Tribochemical wear can be characterized by rubbing contact between two solid surfaces that react with the environment. The corrosive environment may be gaseous or liquid. The wear process proceeds by continual removal and formation of new reaction layers on the contacting surfaces, for example, the oxidative wear.
A refined version of this wear model was developed in which the surface topography was described as a Gaussian distribution of conical asperities [60]. The analysis resulted in the following equation for the wear volume ($W$)

$$W = \left(\frac{\pi \beta A_o}{(4 \tau \nu)}\right) F(P, H, \phi),$$

(5)

where $A_o$ is the apparent area of contact, $\tau$ is dependent on materials properties, $\nu$ is the sliding speed, $P$ is the applied load and $H$ the hardness. $\phi$ is the distribution function of the asperities on the surface and $F(P, H, \phi)$ is a function of $P$, $H$ and $\phi$. $\beta$ is also a function of $P$, $H$ and $\nu$. $\beta$ is a function of temperature and related to the temperature by an Arrhenius relationship:

$$\beta = \beta_0 \exp\left(-\frac{Q}{RT}\right)$$

(6)

where $\beta_0$ is the Arrhenius constant for the reaction, $Q$ is the activation energy associated with the oxide and $R$ is the gas constant. On the basis of simple model for asperity temperatures [61], the surface temperature, $T$, can be related to $P$, $H$ and $\nu$ as follows

$$T = T_0 + f P \nu / [4 J(k_1 + k_2) a]$$

(7)

where $T_0$ is the ambient temperature, $f$ is the friction coefficient, $J$ is Joule's constant, $k_1$ and $k_2$ are the thermal conductivities of the two bodies and $a$ is the radius of the contact area.
This model is dependent on the chemical nature of the surface, mechanical and thermal properties of the materials, micro and macro-geometrical features of the two surfaces and operating conditions (such as load, speed and environment).

2. Friction and wear of modified surfaces

Two major types of modified surfaces have been developed for tribological purposes: hard surfaces for the reduction of wear; and soft surfaces for the reduction of friction forces.

Hard surface layers Hard coatings or surface layers obtained by specific techniques act as wear-resistant layers. When the surface layers are very hard (H > 2000-3000 kg/mm²), the wear rate even under severe conditions can be significantly reduced. Coatings or surface layers with thickness of 1 to 10 μm, which is well below the dimensional tolerance specified for most components, are sufficient for most applications. The selection of the appropriate surface modification method is based on the identification of the primary properties that a wear-resistant material must possess.

According to adhesive wear theory, the wear rate (W), defined as worn volume per unit sliding distance, is proportional to the load and inversely proportional to the hardness of the softer rubbing material. Abrasive wear models also lead to a similar equation in which the wear volume is inversely proportional to hardness. In both adhesive and abrasive wear situations, wear volume per unit sliding distance is therefore adequately described by a general equation of the form:
where \( k^* \) is a proportionality constant. The hardness (or the yield pressure) is seen to be a factor of prime importance in both cases. Experimental results [62] have verified the relationship between the hardness of materials and wear-resistance (Figure 2, for cast iron). It is also known that the hardness and yield pressure are related through a constant of the order of 3 for metallic materials. For non-metals with a much smaller elastic modulus, the hardness is a smaller multiple of the yield pressure.

Based on empirical observations of high wear resistance in materials with large \( H/E \) ratios, where \( E \) is the Young's modulus, Oberle [63] has reported a correlation between wear resistance and \( H/E \) ratio and suggested that materials with low elastic modulus would accommodate the passage of abrasive across their surface through elastic deformation and thus avoid permanent damage. The elastic modulus \( E \) therefore also has a role in wear resistance.

Fundamental aspects of adhesive and abrasive wear indicate that hard coatings or modification for hardening of surfaces are necessary for wear protection. By examining abrasion, wear is found to be a function of the hardness ratio \( H_a/H_m \), where \( H_a \) is the hardness of abrading particles and \( H_m \) that of the abraded material. Little or no wear in the hardness ratio range of 0.72 to 1.12 has been reported [64]. It was suggested that hardness ratio of 0.4 order is desirable to obtain negligible wear [65]. Some hard coatings for tribological applications are listed in Table 1. Microhardness values of these materials are tabulated in Table 2.
Figure 2  Effect of hardness on wear-resistance of cast irons.
Table 1  Hard compounds for tribological applications.

<table>
<thead>
<tr>
<th>Carbides</th>
<th>Nitrides</th>
<th>Oxides</th>
<th>Borides</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiC</td>
<td>TiN</td>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>TiB&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>H</td>
<td>HfN</td>
<td>HfO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>HfB&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>ZrC</td>
<td>ZrN</td>
<td>ZrO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>ZrB&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>TaC</td>
<td>TaN</td>
<td>Ta&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>TaB&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>VC</td>
<td>VN</td>
<td>V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>VB</td>
</tr>
<tr>
<td>NbC</td>
<td>NbN</td>
<td>--</td>
<td>NbB&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>Cr&lt;sub&gt;3&lt;/sub&gt;C&lt;sub&gt;2&lt;/sub&gt;, Cr&lt;sub&gt;7&lt;/sub&gt;C&lt;sub&gt;3&lt;/sub&gt;,</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cr&lt;sub&gt;2&lt;/sub&gt;Cr&lt;sub&gt;6&lt;/sub&gt;</td>
<td>CrN</td>
<td>Cr&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>--</td>
</tr>
<tr>
<td>SiC</td>
<td>Si&lt;sub&gt;3&lt;/sub&gt;N&lt;sub&gt;4&lt;/sub&gt;</td>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>--</td>
</tr>
<tr>
<td>WC, W&lt;sub&gt;2&lt;/sub&gt;C</td>
<td>--</td>
<td>--</td>
<td>WB</td>
</tr>
<tr>
<td>Mo&lt;sub&gt;2&lt;/sub&gt;C</td>
<td>--</td>
<td>--</td>
<td>MoB</td>
</tr>
<tr>
<td>--</td>
<td>AlN</td>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>--</td>
</tr>
<tr>
<td>TiC-TiN(a)</td>
<td>TiN-TiC(a)</td>
<td>TiC-Ti&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;4&lt;/sub&gt;(a)</td>
<td>--</td>
</tr>
<tr>
<td>TiC-VC(a)</td>
<td>(Ti, V)N(a)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Ti-Si-C(a)</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>(Fe, Mn)&lt;sub&gt;3&lt;/sub&gt;C(a)</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>--</td>
<td>(Si, Al)N(a)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>--</td>
<td>Fe&lt;sub&gt;4&lt;/sub&gt;N</td>
<td>--</td>
<td>--</td>
</tr>
</tbody>
</table>

(a) Complex coatings
Table 2  Microhardness values of typical hard coating materials.

<table>
<thead>
<tr>
<th>Element</th>
<th>Carbide</th>
<th>Nitride</th>
<th>Boride</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boron</td>
<td>3700</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Chromium</td>
<td>1600 (Cr$_2$C$_3$)</td>
<td>2200</td>
<td>1800</td>
</tr>
<tr>
<td></td>
<td>1300 (Cr$_3$C$_2$)</td>
<td>1083 (CrN)</td>
<td></td>
</tr>
<tr>
<td>Hafnium</td>
<td>2270 - 2650</td>
<td>1640</td>
<td>2250 - 2900</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>1800 (MoC)</td>
<td>---</td>
<td>2350</td>
</tr>
<tr>
<td>Niobium</td>
<td>2400 - 2850</td>
<td>1369 (NbN)</td>
<td>2100 - 2400</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1720 (Nb$_2$N)</td>
<td></td>
</tr>
<tr>
<td>Silicon</td>
<td>3500</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Tantalum</td>
<td>1800 - 2450</td>
<td>1200</td>
<td>2450 - 2910</td>
</tr>
<tr>
<td>Titanium</td>
<td>2000 - 3200</td>
<td>1200 - 2000</td>
<td>2200 - 3500</td>
</tr>
<tr>
<td>Tungsten</td>
<td>2100 - 2400</td>
<td>---</td>
<td>2400 - 2660</td>
</tr>
<tr>
<td></td>
<td>1450 (W$_2$C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vanadium</td>
<td>2460 - 3150</td>
<td>1520 - 1900</td>
<td>2070 - 2800</td>
</tr>
<tr>
<td>Zirconium</td>
<td>2360 - 2600</td>
<td>1150</td>
<td>2250 - 2600</td>
</tr>
</tbody>
</table>
Another purpose of a hard surface layer is to increase the rolling contact fatigue (RCF) resistance. Bearing components used in most tribosystems involve a rolling and/or sliding motion. The contact area of these components is subjected to repeated high compressive and shear stresses. Recent studies with many types of bearing materials have revealed that the major causes of fatigue failures were due to the properties and characteristics of the contacting surfaces and bulk properties of the bearing materials [66]. Surface degradation mechanisms such as wear, corrosion and oxidation were also found detrimental to the fatigue life of bearing components.

Dill et al. [67] evaluated the RCF behavior of double layer coatings of TiC and CrC prepared by CVD as well as TiN coatings produced by sputter deposition, on a number of bearing steels. Davis [68] studied the RCF behavior of ion plated chromium (with thickness 0.2 - 5 μm) on 440C bearing stainless steel and found that only the films below 0.3 μm thickness resulted in improvement. The RCF properties of hard TiN coatings were evaluated by Hochman et al. [69], using the substrates M50, AMS5749 and 440C martensitic stainless steel. The test results showed that remarkable improvements in endurance life could be obtained with hard films with thickness a little higher than the surface roughness (0.3 - 0.4 μm).

Surface modification can also change the substructure in the near-surface region, therefore, has the potential of influencing the fatigue crack initiation process and thereby significantly increase the total fatigue life. Fatigue crack initiation is generally delayed by limiting plastic deformation (i.e., strengthening), by eliminating deleterious inclusions, or by creating a compressive residual stress in the surface layer. Strengthening may be accomplished by mechanisms such as precipitation, development of solid solutions and
supersaturated or amorphous structures at the near-surface region and grain size refinement. These mechanisms can be affected by surface modification processes. For example, implantation of C in Ti-6Al-4V at 75 keV and a dose rate of $3 \times 10^{17}$ atoms/cm$^2$ was found to produce carbides when the solubility limit was exceeded [70]. At the same time precipitates and lattice defects were also generated by ion implantation. These defects not only produce local strain, but interact with mobile dislocations. Thus, the implantation-induced lattice defects can suppress the mobility of dislocations and produce a strengthening of the surface layer, thereby improving fatigue life.

Surface modification can also influence the stress state in the surface layer. Kumar et al. [71] have shown the beneficial effect of compressive residual stress produced by introducing Al atoms in β-Ti and Al and Cr in polycrystalline copper. Surface alloying may also affect the cyclic deformation characteristics. Charkrabortty et al. [72] proposed that surface alloying with substitutional atoms (Al, Cr) in single and polycrystalline copper leads to the lowering of the stacking fault energy (SFE) which reduces the tendency for cross-slip. This may improve the reversibility of cyclic deformation and make the formation of microcracks more difficult in strain-controlled low-cycle fatigue life.

The selection of coating and surface modification process for wear-resistance should be based on the hardness, adhesion and friction coefficient of resultant surface layer and other relevant properties such as thermal expansion coefficient and thermal stability.

**Low shear strength films** Solid materials such as Teflon, MoS$_x$ and graphite are applied as lubricants on rubbing surfaces. The mechanism of lubrication involves a
reaction between certain molecules in the oil and the surface to form low shear strength metal soap which can provide the lubrication function. In addition to this reaction, extreme pressure additives (usually organic and disulfides) and anti-wear additives (Tricresyl Phosphate) are proposed to form reaction films which contribute additional lubrication functions. After long periods of operation under certain conditions, oxidation and polymerization of the lubricants can take place which produce a soft surface film. In addition to these in situ reaction films, a variety of lubricant adjunct films are put on the surface to accomplish one function or another. These films include soft metal plating, polymer films, reaction films such as oxides, phosphates, chromates and various organic coatings. Another instance of lubrication with low shear strength solids is the preferential accumulation of certain atoms at the sliding interfaces of alloys (e.g., lead) which improves their machinability and makes them better bearing alloys. In fact, it has been proposed that high pressures associated with concentrated contacts solidify the fluid lubricant so that even the so-called fluid film lubrication is really lubrication with a soft low shear strength solid.

A large number of compounds have been found to be able to act as solid lubricants, as listed in Table 3. The only common element that these materials possess is that they are soft. The conditions to make a good solid lubricant film can be summarized as: i) strong adhesion to at least one surface; and ii) a low energy plane either at the surface or in the coating material. The plane can be either inherent in the coating material, generated by adsorption, or by sliding. For example, tribological studies on ion-assisted deposited silver films on ceramic substrates showed that the low shear
Table 3  General types of solid lubricants.

<table>
<thead>
<tr>
<th>Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Organics</td>
<td>Soaps, fats, waxes</td>
</tr>
<tr>
<td>Polymers</td>
<td>Teflon, polyethylene, methacrylates</td>
</tr>
<tr>
<td>Metals</td>
<td>Indium, tin, lead, silver</td>
</tr>
<tr>
<td>Inorganics</td>
<td>AX, AX₅, oxides, sulfides, chlorides</td>
</tr>
<tr>
<td>Glasses</td>
<td>B₂O₃, Pb-SiO₂, PO₄</td>
</tr>
</tbody>
</table>

Figure 3  Schematic representation of the effect of film thickness on the coefficient of friction of low shear strength metallic films on steel.
strength and adhesion of silver coating on the substrate provided low coefficient of friction [73].

In thin film lubrication, the film thickness has a very pronounced effect on the coefficient of friction, as shown in Figure 3 [74]. This behavior can be divided into two regions, namely the ultrathin and the thin film regions, with the effective or critical film thickness at the lowest value of the coefficient of friction. In the ultrathin region, the increase in the coefficient of friction is associated with a breakthrough in the film by mating asperities. In the thin film region, as the film thickness increases, the load-carrying capacity of the substrate surface decreases and an increase in the apparent area of contact leads to a higher friction.

C. Tribological Behavior of DLC Films

Recently, DLC films have elicited considerable attention due to their high wear resistance, optical transparency, and electronic conductance. These films possess several unique characteristics that govern their tribological properties, particularly their high hardness and lubricating nature. In addition, their high thermal conductivity, low thermal expansion coefficient, and chemical inertness have brought them into the foreground of many research programs. The advent of techniques such as hot filament (HF) CVD [75] and microwave (MW) plasma-assisted (PA) CVD [76] have escalated the consideration of DLC films as wear barrier for many moving mechanical assemblies. The main difficulty that has not been overcome is the poor adhesion between the films and their substrates, which restricts the universal applications of these films as wear resistant surfaces.

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1. Deposition methods

The different methods used to produce DLC films can be mainly divided into two groups, high temperature CVD and low temperature ion-beam assisted deposition. The former are based on the chemical decomposition of a carbon bearing gas phase on the growing film surface. The latter methods are performed at temperatures generally between 300-700 K, and, based on the nature of the carbon source, they can be further subdivided into: (i) methods where solid carbon is used as the source material and include carbon beam method, sputtering dual beam method, dc- and rf-plasma sputtering, carbon evaporation combined with ion beam, co-axial (pulsed) plasma method, etc.; and (ii) methods where hydrocarbon gas is the source of carbon atoms, such as dc- and rf-plasma deposition and ionized hydrocarbon beam deposition;

In group (i) methods, carbon is collected onto the surface as neutral atoms and/or ions. In the carbon beam deposition, carbon ions and neutrals are sputtered from a graphite target (cathode) using inert gas sustained glow discharge. The mixture of ions and neutrals is extracted using an appropriate bias voltage. In sputtering dual-beam method, film deposition occurs with carbon atoms either sputtered from a graphite target or evaporated from graphite utilizing a laser beam while at the same time an Ar+ beam is bombarding the surface. Additional H2 gas can be fed to the deposition atmosphere or ion source to produce a-C:H. In these methods, inert gas ions (Ar+) bombard the growing surface and a few at.% of the inert gas may be incorporated in the layer. In the pulsed plasma method, low energy C+ (5-10 eV) in a high density plasma strikes the substrate surface to produce the film.
In group (ii) methods, the substrate is bombarded with various ionized hydrocarbon molecules, neutrals and inert ions (Ar+) with ion energies typically below 1 keV. The deposition process is generally dependent on the gas pressure, power density, bias voltage, ion energy, etc.. In the ion-beam method, the hydrocarbon ions are produced in a separate ion source and the ion energy and the angle of incidence are independently controlled. In these methods, hydrogen is always incorporated in the films.

Some of these processes are summarized in Table 4 [77]. The hydrogen content of the films can vary between 0% and 65%. Most deposition processes also use some ion bombardment of the coating during deposition, which affects film density and structure. The mechanical properties of the films depend on both of these factors.

2. Characterization and atomic structure model

Crystalline carbon occurs in two major allotropes, diamond and graphite. These two forms have different structure and thus quite different properties. Diamond crystallizes on the diamond cubic structure (face centered cubic) and its lattice is extremely dense (3.5 g cm\(^{-3}\)) and strongly bonded. Each carbon atom is bonded by covalent bonds to four other carbon atoms in a tetrahedral geometry (\(sp^3\) bonding). Graphite is composed of hexagonal rings. Each ring is built by a carbon atom with three nearest neighbors arranged in an equilateral triangle (\(sp^2\) bonding), which is much less dense (2.6 g cm\(^{-3}\)) than diamond. Diamond is a metastable carbon form that exists owing to the slow transformation kinetics.
Table 4  Deposition processes for DLC films.

<table>
<thead>
<tr>
<th>Process from hydrocarbon gases:</th>
<th>PACVD</th>
<th>Direct ion beam</th>
<th>Ion plating</th>
<th>Arc</th>
<th>IBAD (Hydrocarbon liquid)</th>
<th>Process from solid C:</th>
<th>Sputtering</th>
<th>Ion beam sputtering</th>
<th>Laser ablation</th>
<th>Vacuum arc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pressure (Torr)</td>
<td>0.01-0.5</td>
<td>$10^{-7}$-$10^{-5}$</td>
<td>0.1</td>
<td>0.75</td>
<td>$10^{-5}$</td>
<td>$&lt;5 \times 10^{-3}$</td>
<td>$&lt;10^{-3}$</td>
<td>$&lt;10^{-6}$</td>
<td>$&lt;10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>Gases</td>
<td>CH$_4$, C$_2$H$_2$</td>
<td>CH$_4$, C$_2$H$_2$</td>
<td>C$_6$H$_6$</td>
<td>Polyphenylether + N</td>
<td>Ar, Ar+H$_2$</td>
<td>Ar+CH$_4$</td>
<td>Ar+H$_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solid target</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>Graphite</td>
<td>Graphite</td>
<td>Graphite</td>
<td>Graphite</td>
<td></td>
</tr>
<tr>
<td>Impurity reactor walls</td>
<td>Filament, walls, gas</td>
<td>grid, walls, gas</td>
<td>Liquid, gas</td>
<td>Gas, target walls</td>
<td>Gas, target walls</td>
<td>Powder, Target walls</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrogen Content (at%)</td>
<td>10-40 (soft), 40-65 (hard)</td>
<td>0-30</td>
<td>&lt;1</td>
<td>~1</td>
<td>5-30</td>
<td>&lt;9</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td>&lt;1</td>
<td></td>
</tr>
</tbody>
</table>

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DLC exhibits extensive sp³ bonding in short range which is thought to be responsible for the diamond-like properties. Hydrogen atoms are usually introduced in its structure because hydrocarbon gases such as methane or acetylene are used to deposit DLC. The hydrogen atoms in DLC structure are thought to stabilize the sp³ bonds [78]. In long range, DLC is predominantly amorphous consisting of small isolated sp² bonded (graphitic) clusters captured in a partially hydrogenated random network of sp³ coordinated carbon. Its detailed structure has been studied using various characterization techniques.

**X-ray diffraction and transmission electron microscopy (TEM)** X-ray diffraction from ion beam deposited DLC has indicated the presence of diamond crystallites in 50-100 Å range. Isolated crystallites up to 5 μm in diameter have been observed [79,80]. With regard to studying the short-range structure, electron diffraction (ED) using TEM is superior to X-rays because the diffraction intensity, sensitive to short interatomic distances, can be observed by electrons. An evaluation of ED patterns of ion beam sputtered carbon revealed that the structures may be identified within an accuracy of 1% as the following metastable carbon phases [81]: i) the cubic diamond (lattice constant a = 0.356 nm); ii) Chaoite, the hexagonal Riescrater carbon (a = 0.89 nm, c = 1.41 nm); and iii) the cubic high-pressure phase (a = 0.555 nm). In an ED study of carbon films produced by rf plasma decomposition of hydrocarbons, the ED patterns revealed d-spacing agreement, within 5% with cubic diamond, except for the presence of forbidden (110) and (211) reflections [82,83]. The ED pattern of carbon films deposited by ionized methane has also been interpreted as a film with diamond crystallites in an amorphous matrix [84,85].

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The evaluation of bright- and dark-field images, along with the ED patterns, can reveal the shape and size of microcrystalline domains in an amorphous phase. For example, in carbon films deposited by condensing ionized benzene, examination of the dark field image showed that the size of the diamond microcrystals was estimated to be ~0.8 nm or several tens of nanometers [86].

**Laser Raman scattering spectroscopy**  Laser Raman spectra are based on the inelastic scattering of optical photons with lattice vibrations and hence provide a useful method for characterizing changes in the translational symmetry of a solid as occurs in small-dimensional crystals. Also, laser photon penetration in carbon is restricted to a short depth (20-50 nm) and this method is valuable for studying the near-surface structure of DLC films.

The first order Raman spectrum for diamond and graphite consists of a single line at 1332 cm\(^{-1}\) (D) and at about 1580 cm\(^{-1}\) (G), respectively [87]. In disordered graphite, where the long-range-translational symmetry is lost, crystal momentum need no longer be conserved and the spectrum changes drastically. The most striking effect is that in addition to G band, another disorder or “D” broad line appears at about 1355 cm\(^{-1}\), which is also associated with in-plane vibrations [88].

The Raman spectra of the as-deposited and laser treated DLC films are displayed in Figure 4 [89]. The spectrum of the as-deposited film shows an asymmetric broad band near 1570 cm\(^{-1}\). In the spectra of the laser-irradiated films, an additional feature appears in the region 1320-1350 cm\(^{-1}\). With increasing laser fluences, both the G- and D- lines become narrower and their relative intensities are changed. This fact has been interpreted as a development of graphitization induced by the irradiation of laser beam.
Figure 4  Raman spectra of as-deposited and laser-treated films at different laser fluences.

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X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) XPS and AES can provide information on bonding energies between atoms and their environment in the near surface region. The bonding energies depend on the chemical state of the atoms involved, and thus represent a key to the study of the basic chemical structures of materials in solid surfaces [90].

There are substantial differences in the chemical bonding of diamond and graphite because of the different coordination—trigonal in graphite and tetrahedral in diamond. High-resolution XPS spectra of atomically clean diamond and graphite were found to have three distinct spectral regions in the valence-bond spectra, as shown in Figure 5. For diamond, region I has a peak between 16 and 21 eV binding energy (zero is the top of the valence band) and arises from s-like bands. Region II has a peak between 10 and 15 eV with a strong mixture of s and p character. Region III has a broad peak between 5 and 10 eV that is attributed to the p bands. For graphite, peak III can hardly be distinguished from the slope of peak II. The XPS spectra of carbon films produced in rf plasma at high deposition rates show a resemblance in region I and III with those of microcrystalline graphite. However, at low deposition rates, the XPS spectra of carbon films demonstrate similarities to the diamond spectra [91].

In AES, the derivative form \( dN(E)/dE \) of the electron energy distribution is used more frequently [90]. The changes observed in the line shape of carbon Auger signals from diamond, graphite and amorphous carbon demonstrate the variety of chemical environments in carbon allotropes, as shown in Figure 6. The line shapes of the carbon Auger signals for the DLC films lie somewhere between those of single-crystal graphite and natural diamond. The observable difference between DLC and graphite is that the
Figure 5  Valence-bond XPS spectra, before (left) and after (right) correction for inelastic losses of diamond, microcrystalline graphite, crystalline graphite and glassy carbon [89].

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Figure 6    Auger spectra of diamond, graphite and amorphous carbon.
shoulder in the DLC film spectrum at 250 eV is not as pronounced as that in the graphite spectrum. The spectrum for natural diamond shows no shoulder and the main peak is shifted to higher energies. However, after sputtering, the spectra from the carbon film and natural diamond become identical with that from graphite [92]. It is thus difficult to distinguish the mixed phases such as graphite, diamond and amorphous carbon in the material.

**The atomic structure model of DLC film** A "defect graphite" (DG) model was developed to describe the structure of DLC in micro-scale [93]. The DG model shows the structure which differs from graphite only in the random distribution of a single type of nonaromatic defect in sufficient density to induce strong π-electron localization. In a perfect infinite graphite sheet without any disorder, π-electrons are completely delocalized and behave as electrons in metals. A defect at which carbon is absent creates a region of low π-electron density. In two dimensions, an arbitrarily small degree of such disorder will induce localization. A higher density of randomly distributed defects will leave only small clusters of closed sp² rings ("aromatic domain"). In other words, a sufficient density of randomly distributed defects confine the remaining aromatic domain to some disconnected "archipelago".

For definition, "aromatic domain" is a connected group of closed, six-sided rings of sp²-coordinated carbon. A nonaromatic defect is a structural defect in the connectivity of the carbon network at a specific site. The nonaromatic defect is the group of nonaromatic rings made by the structural defects and is always much larger than the defect itself. Figure 7 shows the shape of nonaromatic defect associated with single or paired vacancies. The open circles indicate hydrogen atoms. In the model,
different defects have the same effects of $sp^2$-coordinated carbon atoms, Figures 7 (a) and (b), and of $sp^3$-coordinated carbon atoms, Figures 7 (c) and (d), respectively. Evidence has been provided showing that "interplanar links" are through $sp^3$ bonding which produces "amorphous diamond", yet contain very little quaternary carbon (carbon atoms bonded to four other carbon atoms). As shown in Figure 7, in hydrogenated amorphous carbon (a-C:H), the main defect is a carbon atom vacancy with each surrounding carbon atom bonded to hydrogen. There is experimental justification for this model. Also, energy conservation arguments suggest that small vacancies in a growing graphite sheet cannot be filled. It was observed that the introduction of neon into the hydrocarbon plasma during film deposition, or deposition at very high bias voltage results in the increasing of number of $sp^3$ bond [94].

Figure 8 demonstrates a 91-ring cluster with 7 carbon vacancies. In Figure 8 (a), with $sp^2$-coordination, each vacancy corresponds to the removal of three aromatic rings from the graphite sheet. Figure 8 (b) shows the same 91-ring cluster and 7 vacancies, but with $sp^3$-coordination, much more aromatic rings are removed from the graphite sheet and only 49 aromatic rings left. The cluster is divided into two smaller aromatic domains. In the presence of hydrogen, the DG model permits $sp^3$-coordination of carbon atoms and predicts a linear increase in the $sp^3/sp^2$ bond ratio with increasing hydrogen content. The upper limit for this ratio is found in diamond which consists of 100% $sp^3$ bonds. As the $sp^3$ bonds increase in DLC its properties approach closer to those of diamond.
Figure 7  The shape of nonaromatic defect associated with single or paired vacancies. (a) a single vacancy with $sp^2$ coordination, (b) nearest-neighbor pair vacancy with $sp^2$ coordination, (c) single vacancy with $sp^3$ coordination, (d) nearest neighbor pair vacancy with $sp^3$ coordination.

Figure 8  Clusters consisting of 91 rings with 7 carbon vacancies. (a) $sp^3$-coordination; (b) $sp^2$-coordination.
3. Mechanical properties and tribological behavior

DLC films possess many attractive properties of engineering importance, including high hardness, optical transparency over a wide range of wavelength, good thermal conductivity, good environmental resistance, for example to aqueous corrosion and good solid lubricity. Due to these properties, DLC films have attracted considerable interest within high-technology industries, such as magnetic hard disks, ball and rolling bearings, high-precision gears, cutting tools, mechanical seals, etc. Certain fundamental properties of DLC are listed in Table 5.

Mechanical properties of DLC films The hardness of hydrogenated DLC films is typically around 10-20 GPa depending on their $sp^2$ to $sp^3$ ratio and hydrogen content. Much higher values are often reported in some papers, these are generally due to the fact that the films are highly stressed. This is illustrated in Figure 9 for DLC coatings deposited by ion beam assisted method under the conditions where the residual stress in the coating is kept low (<500 MPa compressive) and high (> 2 GPa) [95]. These films contain about 15% hydrogen. In both cases, the hardness measured using a nanoindenter is considerably lower than the hardness measured at the moment of unload owing to the elastic recovery of the system which reduces the size of the indentation. Furthermore, the high stress film is harder than the low stress film (Figure 10). This difference is considerably magnified on unloading showing that stress relaxation is influencing the indentation and elastic recovery processes. The residual stress in ion beam deposited DLC films increases with the energy, ion mass and flux of ion bombardment [96].
Table 5  General properties for natural diamond, diamond coating and DLC films.

<table>
<thead>
<tr>
<th>Property</th>
<th>Natural</th>
<th>Polycrystalline diamond</th>
<th>Diamond-like carbon</th>
<th>Hydrogenated diamond-like carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microhardness (kg/mm²)</td>
<td>10,000</td>
<td>8000 ~ 10,000</td>
<td>~ 5000</td>
<td>3000 ~ 5000</td>
</tr>
<tr>
<td>Resistivity (Ω-cm)</td>
<td>10^13 ~ 10^14</td>
<td>10^8 ~ 10^13</td>
<td>10^11 ~ 10^12</td>
<td>10^7</td>
</tr>
<tr>
<td>Thermal conductivity (W/mK)</td>
<td>900</td>
<td>700</td>
<td>75</td>
<td>7</td>
</tr>
<tr>
<td>Refractive index</td>
<td>2.4</td>
<td>2.3 ~ 2.4</td>
<td>&gt; 2</td>
<td>1.8 ~ 2.1</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>3.5</td>
<td>3.2 ~ 3.4</td>
<td>2.36</td>
<td>1.7 ~ 1.8</td>
</tr>
<tr>
<td>Friction coefficient</td>
<td>0.1</td>
<td>--</td>
<td>~0.1</td>
<td>--</td>
</tr>
<tr>
<td>Chemical resistance</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
<tr>
<td>Visible and infrared transparency</td>
<td>High</td>
<td>High</td>
<td>High</td>
<td>High</td>
</tr>
</tbody>
</table>
Figure 9  
Nanoindentation hardness of 1 μm DLC film on ASP 23 steel under load and unloading as a function of residual stress in the film.
Figure 10  Load-displacement curves for (a) low stress DLC film, (b) high stress DLC and (c) ASP23 substrate.
The hardness and elastic modulus of rf PACVD DLC films (measured by nanoindenter) exhibit a maximum at 200 V applied bias, as shown in Figure 11 [97]. At bias voltages less than 200 V, more hydrogen was found in the film. The highest value of the $sp^3/sp^2$ ratio was determined for the maximum hardness. All these films have high hydrogen contents (above 30%). It is noted that the measured hardness is about one-tenth of the elastic modulus which is near to the theoretical fracture strength of materials ($E/10$) [98]. It thus seems that the hardness of DLC films depends on the separation of atomic planes by microfracture.

Control of residual stress in DLC films is very important because a highly stressed coating shows poor adhesion on its substrate. Since DLC film is chemically inert, it does not intrinsically have good adhesion to many substrates. Carbide-forming elements exhibit the best adhesion for DLC films and they are usually used as interlayers for the films. For instance, introducing silicon into the interfacial regions of DLC films promotes adhesion onto metallic substrates. This may be achieved by a sputtered Si/SiC interlayer or by adding saline to the reactive gas in the early stages deposition [99]. Alternatively, initial evidence has shown that the well developed graded interfaces give the best adhesion up to date [100].

The mechanical properties of hydrogenated and hydrogen-free DLC have been shown to be dependent on temperature [101]. The hardness and elastic modulus of the hydrogen-free DLC films are higher than those of the hydrogenated material in the as-deposited state, but reduce considerably on annealing. Hydrogenated DLC is relatively stable up to around 300°C, until phase transformation due to hydrogen loss.
Figure 11  Nanoindentation measurement of a-C:H films as a function of bias showing hardness (●) and elastic modulus (○).
Tribological behavior of DLC films  The friction coefficient of DLC films against other materials depends on the hydrogen content and the environment as well as other additions to the films.

For hydrogenated DLC films, the friction coefficient varies between 0.1 and 0.2 in wet air and drops to 0.03 in dry nitrogen and can vary between 0.02 and 0.07 in vacuum [102-106]. Hydrogen-free DLC films are less susceptible to the effects of humidity. Low friction is generally produced by the surfaces which are hydrogen terminated, but oxygen or water termination leads to high friction [107]. These hydrogen atoms can come from the environment or from the films if they are sufficiently mobile. In the environment of water or oxygen, the friction coefficient of DLC films will be higher than 0.1. In vacuum or dry inert gases, the hydrogen incorporated in the film can become increasingly important if it diffuses to the surface and maintains hydrogen termination at the worn surfaces. With some types of counterface material, the friction of DLC films depends on the formation of transfer layers during wear which can act to increase or decrease the friction depending on the wear couple. Under fretting conditions, humidity plays an important role during friction of DLC film [108], because a carbonaceous transfer layer with graphite character is formed and the friction can be reduced.

Previous studies reported on methods to reduce the humidity sensitivity of DLC films by producing films containing small amounts of metals by reactive sputtering. It has been found that the films containing about 15% metal have less humidity degradation (friction coefficient is between 0.15 and 0.2 in air with 10% relative humidity) [109-112]. Additions of silicon to the coating gave improved performance with low friction.
coefficients (<0.1) measured in both humid and dry conditions. It was thought that at high humidity, silica sol was formed on the DLC surface which can reduce friction coefficients [109].

Generally, the wear rates for DLC films are as low as \( \sim 10^{-15} \text{m}^3/\text{Nm} \). Addition of metals or other elements such as silicon into the films can lead to further reduction in wear rate [113]. Experiments have shown that these elements can improve the adhesion between DLC films and their substrates. This fact can be indicated in Figure 12 for the case of friction between DLC film and 52100 steel in humid air. The importance of adhesion on wear life of DLC films was further demonstrated by the fact that the wear rate of DLC films against aluminum depends on the deposition temperature which determines the level of residual stress in the films [114]. Other studies have found that the failure of DLC films during friction is due to spalling which is the result of poor adhesion onto the substrates [108].

Spalling of DLC films during friction is initiated by through-thickness cracking. Once such cracks form, they can easily propagate along the interface, particularly if there is a large hardness and elastic modulus mismatch between the film and substrate. The hardness of the substrate is critical in the wear behavior of DLC films, as shown in Figure 13. Thus, a hard substrate or surface layer is necessary for the good performance of DLC films.

**Wear mechanisms of DLC films** Various theories have been proposed to explain the tribological behavior of DLC films. Hirvonen, *et al* [115] suggested that the low steady-state friction coefficients of DLC films observed at large sliding distance during lifetime tests were related to the formation of a carbon-rich transfer layer on the
Figure 12  Friction measurement in pin-on-disc wear tests of normal and silicated DLC on an ASP23 substrate.

Figure 13  The worn volume of the film as a function of load in the scratch test for ion beam deposited DLC films on soft mild and tool steel.
counterface. In an alternative mechanism, the low friction coefficients of DLC (α-C:H) films during sliding were attributed to the two-stage pyrolysis of organic material into graphite [116], which includes carbonization (loss of hydrogen) and polymerization occurring between 400°C and 600°C. It has also been proposed that the occupation of the dangling bonds on the surface of the DLC films by oxygen and hydrogen reduces the possibility for the formation of bonds between DLC film and its counterface, which creates the low friction force [117]. Support for this mechanism has been provided by tribological experiments carried out between PTFE and DLC films. Finally, chemisorption of hydrogen and/or other chemically active species [118-120] and formation of a double-layer structure and/or micrographitization [121,122] on sliding interfaces have been proposed to explain the frictional behavior of DLC films. Thus, a controversy exists at present and the actual wear mechanism of DLC films is still not well understood.

D. Graded or Composite Interfaces and FE Modeling for Stress Analysis

1. Graded or composite interfaces

Graded or composite interfaces are characterized as composites owing to their microscopically inhomogeneous character. Continuous change in composition results in a gradient in the properties of the graded or composite interfaces. The graded or composite interfaces were developed to satisfy some purposes including resistance to thermal shock [123-127], optical and/or electronic applications [128]. Also, some composite interfaces such as laminated Al/Cu, Ti/TiN, etc. were designed for the modification in mechanical properties of the surfaces [129,130]. According to Koehler's
theory [131], a thin-layered metal-A/metal-B laminate, in which A has higher dislocation-line energy and metal B has lower dislocation-line energy, will have significantly higher strength than either A or B alone. It was found that in laminated Al/Cu layer, for layer thickness < 70 nm (the critical thickness), the yield stress of the layer is 4.2 times higher, and the tensile fracture strength is 2.4-3.4 times higher than the values given by the rule of mixture for Al and Cu [129].

DLC films usually have poor adhesion to the substrate and graded or composite interfaces with gradient properties are expected to have a positive impact on DLC behavior. Graded or composite interfaces have previously been used to produce high quality DLC films [132]. Unbalanced magnetron sputtering has been used [133] to deposit composite coatings of TiN, TiCxNy, TiC, CrN, (TiCr)N, (TiCr)CN, (TiCr)C, metal doped Ti_x%-DLC on 316 stainless steel substrate. It was found from scratch tests that DLC with the composite interface exhibits high critical load (60 N), which was attributed to the layered structure in composite interface with gradient properties, stress relaxation and good coating elasticity. Low friction coefficients of 0.15-0.18 were measured in friction tests. Also, DLC film with composite interface (Ti, TiN, TiCN, and TiC) was produced by the same method mentioned above. It was found that the DLC film showed a microhardness value exceeding 39 GPa and excellent adhesion properties with a critical load value of 110 N [134].

In brief, previous experimental results show that the provision of graded interfaces has an important impact on the fundamental behavior of DLC films and possess the potential to enhance adhesion and improve their tribological behavior. In spite of the importance of this issue, no investigation has been conducted on the
tribological behavior of DLC films with graded or composite interfaces and more importantly no study has been performed to explore the corresponding fundamental wear mechanism.

2. Stress/strain distribution in layered surfaces

The microscopical inhomogeneity of a layered surface creates non-uniform stress and strain distributions. During indentation and friction, the degradation of hard coatings largely depends on the non-uniform spatial stress distribution and the plastic flow in the coating/substrate. Due to the difference in mechanical properties between the coating and substrate, accurate solutions of stress distribution in layered media cannot be extracted from previous work on homogenous media. Proper analysis then requires advanced numerical methods such as finite element (FE) methods.

Early investigations have produced profound information about the deformation characteristics of sliding contact on both layered and homogeneous media. Hamilton and Goodman performed both plane-strain and three-dimensional analysis of rigid circular sliders contacting a homogenous half-space [135]. It was found that the maximum von Mises stress, and hence the point of initial yielding, occurred in the subsurface directly below the slider for a sufficiently low friction coefficient, and it was moving toward the surface with increasing friction coefficient. From the crack initiation viewpoint, Kennedy and Ling used FEM to analyze the indentation problem of a thin elastic-plastic coating deposited on different substrates [136]. They showed that the indenter size, the contact pressure, the coating thickness, and the coating and substrate properties affect the yielding event.
Considering frictional forces on the coating surface, King and O’Sullivan [137,138] analyzed two- and three-dimensional quasi-static stress states by using the least squares approach and determined the distribution of von Mises stresses in the coating and substrate. It was found that the position of the maximum von Mises stress depends on the stiffness of the coating relative to the substrate, the ratio of coating thickness to half-contact width and the value of the coefficient of friction.

A more rigorous analysis has been performed by Komvopoulos [139] using FEM to calculate the stress distribution of an indented hard coating (elastic modulus $E_c = 400$ GPa, Possion's ratio $\nu_c = 0.3$, yield strength $\sigma_y = 6.86$ GPa) on a metallic substrate ($E_s = 100$ GPa, $\nu_s = 0.3$, $\sigma_y = 1.0$ GPa). It was shown that yielding always appears at the coating/substrate interface under critical contact conditions (von Mises yield criterion [140]) for the combination of coating and substrate, and the plastic zone does not grow toward the surface of the indented layered medium, but is restricted to the boundary of the hard coating and substrate. The analysis also gives a deformation map for the estimation of the transformation from elastic deformation to elastic-plastic deformation, as shown in Figure 14 which represents the elastic-plastic boundary as a function of $h/R$ and $d/R$ (where $h$ is the thickness of the coating, $R$ is the radius of indenter and $d$ is the half width of contact area) and can be used to determine the location and thickness of the plastic zone.

Similar FE analysis of a rigid indenter on an elastoplastic two-layered system has been conducted by other investigators [141,142]. The Hertz theory and FEM have been combined by Djabella and Arnell to analyze elastic stresses in single, double and multilayer system [143]. More recently, the surface deformation characteristics resulting

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Figure 14  Position of elastic-plastic boundary along the depth-direction.
from indentation and sliding contact between a rigid sphere and a layered half-space were examined by performing three-dimensional FE simulations [144].

Detailed local yield maps for the indentation and friction of coating/substrate systems were developed by Diao and Koji [145]. The positions of yielding initiation under different conditions are shown in Figures 15 (a) and (b). For low friction conditions ($f = 0.25$, Figure 15 (a)), local yielding occurs in the substrate under a wide variety of $\sigma_l$, $\sigma_n$ values when $t \cdot a < 0.3$ ($t =$ film thickness, $a =$ half contact width). Only when $\sigma_l$, $\sigma_n$ is very close to unity and $t \cdot a > 3$, the local yielding appears inside the coating. Between these two cases, the yielding starts at the coating/substrate interface and develops into the substrate. For high friction condition ($\mu = 0.5$, Figure 15 (b)), the yielding at the surface dominates when $\sigma_l$, $\sigma_n < 3$ and the yielding at the coating/substrate interface dominates when $\sigma_l$, $\sigma_n > 3$. It can be concluded that the yielding mostly occurs at the coating/substrate interface and it becomes predominant at the surface as $f$ and $t \cdot a$ are larger. The yielding starts moving into the substrate when the coefficient of friction is low.

The above analyses indicate that under certain external loading condition, plastic flow will be developed at the hard coating/substrate interface. Usually, for a brittle coating (such as DLC), plastic flow near or at the interface may initiate nucleation and growth of cracks along the interface due to its inability to follow the deflection of the substrate. The interfacial delamination of the coating is expected, generated by this plastic flow and followed by crack growth along the interface. Thus, yielding on the coating/substrate interface should be avoided.
Figure 15 Local yield map as a function of $Y_f$, $Y_s$, and $\nu/a$ under low friction (a) and high friction (b).

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DLC films possess high hardness and low friction ($f = 0.02-0.2$) [102-106].

According to the previous analyses (Figure 15 (a)), in order to avoid the yielding on the coating/substrate interface, the deposited DLC films should be very thick ($t/a > 3$) or very thin ($t/a < 0.3$). However, the intrinsic highly compressive stress (> 4 GPa) usually present in DLC coatings and their brittle nature can trigger the initiation and growth of cracks within the coatings [146,147]. Thus, as the coating thickness increases, the stored elastic strain energy builds up to a critical level that can cause either coating delamination from the substrate or cracking of the coating itself. As a result, deposition of thick DLC coatings is not recommended.

Under the conditions of thin hard DLC film, yielding is anticipated to evolve in the substrate in the vicinity of the substrate/film interface, substrate hardening is thought to exercise an important effect on the tribological behavior of the DLC coating. The nitriding process offers the opportunity to produce this surface strengthening of the substrate. Figure 16 shows the composition profile of surface nitrided Ti-6Al-4V alloy, and Figure 17 is hardness profile of the IPAP processed Ti-6Al-4V alloy [153]. Thus, this process is anticipated to cause a major shift on the tribological behavior of DLC films. The issue has not been investigated yet and is one of the major objectives of the present investigation.
Figure 16  The relationship between Ar⁺ sputtering time in Auger analysis and nitrogen concentration.
Figure 17  Microhardness profiles of the surface layers of ion implanted and IPAP processed Ti-6Al-4V alloy.

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IV. EXPERIMENTAL

A. Materials

Various materials were utilized in the present work as substrates for the deposition of DLC films. First, several DLC coated specimens were available through collaboration with Argonne National Laboratory (ANL) and they were used for the DLC wear mechanistic studies. More specifically, three DLC-coated metallic disc materials have been involved in this work, M50 steel (8.3 GPa hardness), AISI 440C bearing steel (8 GPa hardness) and Ti-6Al-4V alloy (4.4 GPa hardness). Balls (9.5 mm in diameter) of M50 steel, 440C steel and Al₂O₃ and cylindrical rods (9.5 mm diameter and a tip radius of 127 mm) of Ti-6Al-4V alloy have been used as counterface pin materials. The availability of different pin and disc materials offered the opportunity to analyze wear debris from these specimens and study the tribological behavior of DLC films as a function of the properties of substrate and pin materials.

The material selection for the investigation of the effect of operational and environmental parameters on tribological behavior of DLC films involved SiC as the disc material and ZrO₂ as the corresponding pin material (9.5 mm in diameter). This particular selection was motivated by the fact that SiC possesses a high hardness (Hᵥ = 22.0 GPa) close to that of DLC and DLC shows excellent adhesion on SiC. Also, the ZrO₂ pin was selected due to its low thermal conductivity (about 1-2 W/mK) in order to reduce the heat dissipation rate at the contacting asperities and allow a greater impact of the effect of operational parameters (sliding velocity and loading level) and environmental parameters (humidity and temperature) on the tribological behavior of
DLC films. The objective of this part of the study is to investigate the effects of testing and environmental parameters on the tribological behavior of DLC films. The selected characteristics minimized possible substrate material effects, while enhancing the influence of the testing and environmental parameters on the fundamental processes occurring during wear.

All ball materials had a surface finish better than $R_a = 0.05 \mu m$. The disc specimens, 50 mm in diameter and 5 mm in thickness, were machined and ground to $R_a = 1 \mu m$ and polished with diamond paste to a surface roughness of $R_a = 0.05 \mu m$. Balls and discs were ultrasonically cleaned in methanol and dried prior to film deposition and/or wear testing.

The Ti-6Al-4V alloy was selected as the substrate material for the development of the duplex treatments. Titanium and its alloys possess excellent strength-to-weight ratio, fracture toughness, corrosion resistance and biocompatibility, but their wear performance is not satisfactory. Thus, there is a current need to improve the wear properties of titanium alloys in order to broaden the field of applications of these alloys. An area of immediate interest is the biomedical field where titanium alloys are used as prosthesis materials for hip and knee replacement. The degradation of these implanted devices is mainly associated with poor wear resistance.

B. Development of Duplex Diffusion/DLC Coating Treatments

IPAP was used to develop the hard nitriding layer in the Ti-6Al-4V substrate. Previous studies have shown that favorable surface conditions had been created on Ti-6Al-4V alloy by IPAP, leading to the formation of desired nitrides, deep diffusion zones
and hence significant improvements in properties ranging from thermal and chemical stability to hardness and wear resistance [153].

A preliminary study was conducted initially to assess the effect of IPAP parameters (voltage and current density) on the produced nitrided surfaces, i.e., resulting surface roughness and microhardness, in order to select desirable (optimal) nitriding parameters. Emphasis was given to identifying conditions that produce low surface roughness, since that is an important parameter in obtaining smooth DLC films. Also, a kinetic study was conducted using the previously selected IPAP parameters in order to develop the relationship between nitriding depth and processing time. Two nitriding depths were developed in the present study in order to investigate the effect of the depth of the hardened zone on the tribological behavior of DLC film.

The experimental system which was used for the production of the duplex diffusion/DLC film treatments is shown in Figure 18. The system was first used in the ion nitriding mode to produce the diffusion layer and then in the IBD mode for DLC film deposition.

Ion nitriding was conducted using a triode glow discharge [153]. Before nitriding, the specimen surface was sputter cleaned by Ar$^-$ at 2000 V accelerating voltage and 50 mTorr partial pressure for 10 min. The nitriding parameters were: cathode voltage: 2000 V, anode bias: 80 V, current density: 1 mA/cm$^2$ and partial pressure of nitrogen: 50 mTorr. The nitriding time was dependent on the required depth of the nitrided zone based on the results of kinetic study. Following nitriding, a thin Si bond layer (about 50 nm thick) was deposited using a magnetron sputtering source. The purpose of the bond layer was to enhance adhesion between the substrate and the DLC.
Figure 18  Schematic depiction of IPAP and IBD system.
film. Previous tests showed that such a Si interlayer resulted in high adhesion strengths (>90 MPa). Finally, the DLC film was developed using the IBD method. A Kaufmann-type, filamentless ion source was utilized and fed with methane, CH₄, the carbon source. The IBD process was carried out at an acceleration energy of 750 eV and a current density of approximately 2.5 mA/cm² resulting in a deposition rate of about 0.1 µm/h. These conditions have been found to produce high quality and adherent DLC films [26]. The thickness of the DLC film in the present work is in the range of 0.4 ~1 µm. It has been established that when dealing with hard films, in order to counteract the effect of substrate roughness, the film needs to be appreciably thicker than 0.1 µm, but not very thick in view of the high compressive stresses in thick films [78]. The optimum film thickness for wear resistance has been estimated to be in the order of 0.4-0.6 µm [155]. Similarly, based on the previous stress field analysis [139, 145] and considering the loading levels of interest (1~20 N) for the pin/disc system of Ti-6Al-4V/DLC the half-contact width is in the range of 0.83~2.25 µm. Thus, the optimum thickness of the DLC films is expected to be in the range of 0.3~0.8 µm.

Another experimental facility used for the deposition of DLC films was a magnetron sputtering system, Perkin-Elmer sputtering system, Model 2400 at ANL. In this deposition system, methane (the carbon source) was fed into the high vacuum chamber. rf energy is utilized in this system to break the bonding in the CH₄ molecule and a bias is applied to the substrate to attract the generated ions resulting in deposition of DLC film. A previous study has shown that the structure and the tribological behavior of IBD CH₄ grown and sputter grown DLC films is compatible [154]. A kinetic study on DLC growth showed that 1 hour deposition can produce DLC coating.
with the thickness of ~0.4 μm. The procedures for sample cleaning and deposition of the Si interlayer were the same as in IBD mentioned above. High purity methane was fed into the chamber and its partial pressure was kept at 21-23 mTorr through the deposition process. The rf forward power during deposition was around 800 W and the bias on the substrates was 500 V.

Finally, DLC films were deposited on Si single crystal and NaCl cleaved crystals, respectively. The film thickness of the DLC film deposited on Si specimens was similar to that deposited on the metallic substrates, whereas electron transparent DLC films of about 50 nm thickness were deposited on NaCl crystal. The latter films were used for the TEM studies.

C. Friction and Wear Experiments

1. Pin-on-disc tribological test

Since tribological properties of materials are mainly described by their friction coefficient and wear rate, wear testing has been designed to measure these two parameters. For surface modified materials, friction coefficient and wear rate were used for comparison of tribological properties between untreated and treated surfaces [148,149].

In the present research, the tribological behavior was investigated by conducting pin-on-disc experiments utilizing a computer controlled pin-on-disc tribometer in order to obtain and study the frictional and wear response. The coefficient of friction was monitored with the aid of a linear variable-displacement transducer and was continuously recorded throughout the tests. First, tests were performed on DLC-coated M50 steel
and Ti-6Al-4V alloy substrates, using mating M50 steel, Ti-6Al-4V alloy and Al₂O₃ pins, respectively. These tests were conducted under 10 N loading level and 0.05 m/s sliding velocity for a total sliding distance of 1000 m, to evaluate the initial friction behavior of the DLC films. Second, long-duration (lifetime) friction tests were conducted on DLC-coated 440C substrates using mating 440C balls under 5 N, 10 N and 20 N loads and at 0.5 m/s to assess the long-term friction of DLC as a function of load.

The average wear rate of the DLC films was calculated by dividing the wear volume (mm³) by the contact load (N) and sliding distance. Calculations of the wear volume of the pin materials were based on microscopic determination of the diameter of the circular wear scars, and assuming a flat wear scar. The wear scar diameter was measured at two vertical directions using an optical microscope and the average diameter (d) was used to calculate the pin wear volume (Wₚ) based on the standard formula:

\[ W_p = \frac{\pi d^4}{64r} \]  

where \( r \) is the pin radius. The wear volume of the DLC film was estimated from the traces of surface profiles taken across the wear track. At least four profiles were taken on each wear track and the average value of the cross-sectional wear trace area was used for the calculation of the wear volume. Initial contact area and stress (mean Hertzian stress) were estimated based on the calculations shown in Appendix 1. At least duplicate tests are conducted for all wear experiments.
2. Investigation of the influence of operational parameters on the frictional behavior of DLC coatings

During friction, the interaction between two surfaces can create temperature rise on the contacting regions, which may induce microstructural changes and phase transformations. On the basis of contacting models, two surfaces contact by asperities. Dealing with thin films and given the small material volume involved in the contacting asperities, it is evident that these changes occurring at asperities play a fundamental role in the tribological behavior. The principal value of temperature rise is mainly related to external load and sliding velocity due to friction-induced heat [150]. Also, depending on experimental parameters, on some individual contacting asperities, the temperature rise can become significant, reaching very high levels, i.e., the flash temperature $T_f$, which can be estimated by equation (7). From that expression, it can be seen that besides inherent materials properties, loading level and sliding velocity are the most important factors which can affect the tribological behavior of materials. Thus, in the present wear experiments, different loading levels and sliding velocities were selected to investigate the effect of these two factors on the tribological behavior of DLC coated surfaces.

The frictional tests between DLC-coated SiC and ZrO$_2$ were conducted, at sliding velocities between 0.06 and 1.6 m/s and under 1 N to 10 N loading levels, in order to study the effect of wear parameters (sliding velocity and loading level) on the tribological behavior of the DLC film. The total sliding distance of the latter tests was 10 km.
3. Investigation on the influence of environmental parameters on the frictional behavior of DLC coatings

In view of previous reports [102-108], humidity is expected to influence the wear behavior of DLC coating by forming a moisture layer on the contact surface. It was also found that higher temperature can accelerate the kinetics for carbonization (loss of hydrogen atoms) of DLC films followed by polymerization [116]. It was revealed that environmental parameters (humidity and temperature) are other important factors which can affect the tribological behavior of DLC coatings. This provided the motivation for present research to study the effect of environmental parameters on the friction behavior of DLC films by applying various levels of humidity and temperature.

Friction tests were conducted under various environmental conditions (humidity: 0% to 100%; temperature: -10°C to 200°C) in order to investigate the environmental influence on the tribological behavior of the DLC coating. Low humidity was created by blowing dry air onto the contact region while high humidity by blowing water vapor onto the contact region. The low temperature was generated by conducting dry ice (CO$_2$) vapor to the experimental environment and the friction test in high temperature environment was completed by setting the testing sample on an electrical heater with pre-determined value of temperature.

4. Tribological investigation of duplex treatments

This part of the experimental effort used DLC/untreated Ti-6Al-4V alloy and DLC/nitrided Ti-6Al-4V for two different nitrided depths. The frictional tests were conducted under loading levels in the 1-5 N range, using Al$_2$O$_3$ as the pin material. The purpose of the variation in the nitriding depth and the loading level during these tests
was to assess the possible correlation between the initial contact stress (extent of yielding), the depth of the hardened zone and the tribological behavior of duplex DLC/nitrided Ti-6Al-4V system.

D. Characterization of Resulting Surfaces and Wear Debris

Continuous contact events at asperities also result in wear products (debris). It was thought that the wear debris bears the signature of the wear process [151]. Surface analytical techniques used in previous studies have shown that debris is usually the mixture of transferred materials from either of the two contacting surfaces and the products of frictional process [152]. So any alteration and/or transformation occurring at asperity contacts during the wear processes can be studied by analyzing the wear debris. Similarly, when dealing with tribology of thin films, the nature of the debris generated carries valuable information regarding the wear process. Thus, debris were characterized after wear testing to study critical processes occurring at asperity contact and get insight into the wear mechanism. For example, some critical questions to be answered are related to the size and nature of the debris that bear information on the film removal process and possible structural or microstructural changes occurring at asperities. During wear of thin films, debris can be formed on the pin surface and/or on the wear track region of the disc. TEM was mainly used to characterize the structure and microstructure of debris generated during wear of DLC films. In addition, other analytical techniques were selectively used for the further characterization of the debris, and this information were correlated to the frictional behavior. A better understanding of
the fundamental wear mechanism of DLC films was developed in light of the above information.

Several techniques were used to characterize the as-deposited DLC films, the duplex diffusion/DLC coating specimens and the wear debris.

Hardness of DLC films was evaluated by taking surface microhardness measurements at various loads using a Knoop indenter. The nitrided specimens were evaluated by taking surface microhardness measurements and the depth of the hardened zone was estimated by developing microhardness profiles as a function of distance from the surface. This is accomplished by using metallographic cross sections of nitrided specimens.

Surface roughness of produced films and nitrided specimens were determined by profilometry measurements utilizing an Alpha Stepper 200 with a resolution better than 0.1 μm (Electrical and Computer Engineering Department, LSU). Profilometry measurements were also taken on wear tracks to assess wear loss after testing.

AES and XPS surface analysis techniques were employed to investigate the composition and chemical bonding states of the produced surfaces. AES and XPS analyses were carried out by using an Auger/XPS electron spectrometer (PHI Model 548). AES was conducted at a background pressure of about $10^{-8}$ Pa with an $E_p = 3$ keV primary electron beam energy, a modulation voltage $V_{\text{mod}} = 6$ eV, an electron beam current $I_p = 20$ mA and an electron multiplier voltage of $V_{\text{mul}} = 1.65$ keV. Relative intensities were determined from peak-to-peak heights, and atomic concentrations were calculated from these intensities by using the appropriate sensitivity factors. For XPS, a 10 keV, 40 mA Mg-Kα X-ray source was utilized for photoelectron ejection from the...
specimen. The C1s peak at 284.6 eV was used as a reference for all detected peak positions. High resolution spectra were obtained in the binding energy range of interest for the various elements.

Scanning electron microscopy (SEM) (ISI-60A) was utilized to observe surface morphology of processed samples. Surface morphology on the atomic level was also characterized by atomic force microscopy (AFM) (Chemistry Department, LSU). SEM was also used to measure the thickness and examine the cross sectional structure and morphology of the produced layers. This was accomplished by flexing to fracture DLC-coated Si wafers and examining the cross section. In addition, SEM was used to examine wear tracks and transfer layers formed on pin surfaces during the friction process.

Analytical TEM (Jeol 100C) with electron diffraction was employed to examine the microstructural characteristics of as-deposited DLC films on Si and NaCl substrates and wear debris. TEM foils were prepared by dissolving the NaCl substrate in water and then lifting the DLC film onto a Cu grid (400 mesh). Also, fine particles of as-deposited DLC films were obtained by scratching the DLC-coated discs using a sharp blade and transferring onto the Cu grids. Similarly, transfer layers on pin surfaces and wear debris from wear tracks were collected by the same method for TEM observations. Analytical TEM was carried out at 100 keV. Bright field and dark field techniques were used to obtain the detailed structure of as-deposited DLC films and wear debris. Electron diffraction was used to analyze the structure and determine lattice parameters of the as-deposited DLC and wear debris.
Laser Raman spectroscopy (in collaboration with the Aristotle University of Thessaloniki, Greece) was used to detect bonding structures and $sp^3/sp^2$ ratio in as-deposited DLC films and wear debris by using an Ar$^+$ laser operated at 514.5 nm, at a power of 30 mW and the range from 900 to 1800 cm$^{-1}$. This method is sensitive to the near-surface region and thus can provide information relating to transformations that may be occurring on wear tracks during friction.

E. FE Modeling of the Yielding Behavior of a Hard Coating/Substrate System with Graded Interface under Indentation and Friction

Up to now, no information related to the yielding behavior of indented graded media (graded yield strength and/or elastic modulus) under friction is available in the literature. One of the objectives of this study, therefore, was to investigate, using FEM, the yielding behavior in a system composed of a hard coating deposited on a graded interface developed in a soft substrate. DLC coating was selected as a model coating. A relatively low $E$ alloy (Ti-6Al-4V alloy) was selected as the model substrate material. As mentioned above, hardness gradient can be produced in this alloy by IPAP that results in a nitrogen diffusion layer. In the model, friction is generated by assuming a rigid steel cylindrical surface sliding on the duplex DLC/nitrided Ti-6Al-4V alloy.

The FE calculations were divided into two groups: (i) a substrate with a gradient in yield strength while the elastic modulus is constant, and (ii) an interface with linearly graded elastic modulus. Results from group (i) calculations were presented as a function of coating thickness, external contact stress, coefficient of friction and elastic modulus of coating, in order to obtain an insight into the influence of these parameters on the initiation/growth of the plastic zone in the substrate during indentation and friction.
Group (ii) calculations were conducted by assuming an array of linearly graded elastic modulus in order to investigate its effect on the stress distribution in the coating/substrate region.
V. RESULTS AND DISCUSSION*

A. Characteristics of As-Deposited DLC Films

The DLC films produced under the present IBD conditions are featureless and very smooth with a mean roughness of $R_a = 0.03 \, \mu m$. The observations at high magnification by AFM showed that the film surfaces are extremely smooth, uniform and rather amorphous, since no evidence of long-range order is revealed. Figure 19 [156]. SEM examinations of fractured cross-sections of DLC-coated Si substrates at high magnifications showed that the films were dense and appeared to be free of bulk volume defects, Figure 20. The Knoop microhardness of as-deposited DLC films was found to be about 30 GPa (under 100 g load).

TEM observations of the as-deposited DLC microstructure show a uniform three-dimensional network structure with a medium-range order present having an approximate average domain size of 25 nm. Figure 21 [156]. The ED patterns exhibit diffuse rings consistent with the amorphous nature of these films. The ED pattern analysis of the two rings present reveals a $d$-spacing of about 0.2 nm and 0.113 nm, respectively. The measured $d$-spacing of the two rings for the as-deposited films is suggesting a diamond-like structure. It should be noted that in crystalline diamond the $(111)$ and $(220)$ are the strongest reflections corresponding to $d = 0.206$ nm and 0.126 nm, respectively. It is interesting to note that the central spot in the ED pattern of as-


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Figure 19 Atomic force micrograph showing typical surface topography of DLC film with a mainly amorphous structure.
Figure 20  Cross-sectional scanning electron micrograph of a typical DLC film deposited on Si substrate.
Figure 21  Bright field transmission electron micrograph from as-deposited DLC film and the corresponding diffraction pattern. The two rings corresponding to the diamond-like structure are indicated by large arrows whereas the diffuse halo is indicated by a smaller arrow.
deposited DLC films is larger than usual. This is more than likely attributed to the strongest (00.2) graphite reflection that appears as a diffuse halo with a \( d = 0.34 \) nm encircling the transmitted beam, Figure 21.

Recently, an extensive study has been conducted to characterize DLC films ion-beam deposited under the same conditions [87]. It was established in the latter studies that the DLC films are composed of a mixture of \( sp^3 \) and \( sp^2 \) carbon bonding. For example, it was determined from IR absorption measurements that the average \( sp^3/sp^2 \) ratio was about 3.6:1. Also, spectroscopic ellipsometry measurements from the present DLC films [87] showed an optical band gap of about 1.6 eV. The latter and present experimental results are consistent with a theoretical model proposed to describe the structure of DLC and explain the relatively low optical band gap observed in these films despite the large fraction of carbon with diamond-like \( sp^2 \)-bonding [93]. According to the above model, \( sp^2 \)-bond carbon atoms tend to segregate in small graphitic clusters containing fused six-fold rings (six to a hundred rings can be involved ) and are interconnected with \( sp^2 \)-bonded random network. According to this model, the graphitic clusters in the present films would contain about 14-15 aromatic rings, a number that seems to be in general agreement with the size of the microstructural features observed in the present study with TEM.

B. Tribological Behavior of DLC Films

1. Friction behavior of DLC coating

The variation of the coefficient of friction during the experiments that were conducted to evaluate the initial friction behavior of the DLC films is shown in Figure
These tribological tests were performed under 10 N loading level and 0.05 m/s sliding velocity for a total sliding distance of 1000 m. An intermittent observation was performed at a sliding distance of 100 m. It can be seen that in all cases there is a break-in period where $f$ has a higher initial value and gradually decreases reaching a plateau region (constant $f$), Figure 22. The duration of the break-in period is marked by arrows on the figure and is also shown in terms of length of sliding distance. The shortest break-in period was observed for the Ti-6Al-4V alloy pin followed by the Al$_2$O$_3$ pin, whereas the M50 pin showed the longest break-in period.

The table in Figure 22 summarizes the wear characteristics for these experiments. Overall, the wear-test results demonstrate that IBD deposited DLC films are quite resistant to wear and impart low friction to sliding. It can be seen that the wear rate of DLC is higher when deposited on a soft substrate (Ti-6Al-4V alloy) compared to a hard substrate (M50 steel) material. Also, the initial wear rate (measured at 100 m sliding distance) is usually higher and is consistent with the higher $f$ value at the initial stages of the wear process. The results also seem to indicate that there is no correlation between the initial mean contact stress (Hertzian stress) and the wear rate. This is due to the fact that during friction the initial morphology and thus contact area existing at loaded asperities is significantly altered. It is broadly accepted that loading level is a more appropriate parameter for this purpose [56].

Examinations after testing show that in all cases large colonies of a carbon-rich transfer layer were present on the surface of the pin material, Figure 23. Even though details were not given, the presence of a transfer layer has been mentioned previously for tribosystems involving metallic and ceramic balls rubbing against DLC films [115, 157-
Calculations of the initial contact area and stress are shown in Appendix 1. NG = negligible

<table>
<thead>
<tr>
<th>Pin on Disc Material</th>
<th>Initial Contact Area (x 10^{-12} m^2)</th>
<th>Initial Contact Stress (MPa)</th>
<th>Wear Rate ($x 10^{-6}$ mm$^3$/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pin</td>
<td>Disc</td>
<td>Pin</td>
</tr>
<tr>
<td>1. M50 on DLC-M50</td>
<td>26</td>
<td>910</td>
<td>NG</td>
</tr>
<tr>
<td>2. Al$_2$O$_3$ on DLC-M50</td>
<td>23.6</td>
<td>1106</td>
<td>NG</td>
</tr>
<tr>
<td>3. Ti-6Al-4V on DLC-Ti-6Al-4V</td>
<td>90.0</td>
<td>76</td>
<td>10.8</td>
</tr>
<tr>
<td>4. Al$_2$O$_3$ on DLC-Ti-6Al-4V</td>
<td>23.6</td>
<td>1106</td>
<td>NG</td>
</tr>
</tbody>
</table>

Figure 22 Variation of the friction coefficient as a function of number of wear cycles. The arrows indicate the end of the break-in stage. ($D_w$ denotes the wear-track diameter, the table above summarizes the initial contact situations and wear parameters in the tests, the numbers next to the arrows indicate sliding distance in meters)
Figure 23 Scanning electron micrograph showing structure and morphology of transfer layer formed on (a) M50 steel, (b) Ti-6Al-4V alloy pin.

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(c) high magnification of transfer layer shown in (b).
It should be noted that examinations in the present study show that traces of a transfer layer are present on all pin surfaces even after 100 m testing suggesting that transfer layer formation started in the early stages of the wear process. The transfer layer exhibited a long strip morphology forming on the wear scars of the pin surface along the sliding direction. Attempts to detach the transfer layer from the pin surface showed that it had a very low adherence to the surface. Also, a relatively thicker transfer layer is found on the Ti-6Al-4V alloy pin surface compared to the other two pin materials (more evident on M50 than on Al₂O₃ surfaces). This seems to be consistent with the observation that the plateau in the frictional test using Ti-6Al-4V alloy pin was reached significantly earlier (about 3,000 cycles or 170 m) compared to the tests using the other two pin materials (from 13,500 to 17,500 cycles or 330 to 560 m).

This behavior can be related to the larger contact surface area and higher initial wear rate expected for this pin material due to its lower hardness. Both of the above factors would be expected to contribute to an easier attachment of the transfer layer on the wear scar of the pin surface by mechanical locking. In fact, the wear scar measurements from pin surfaces after 100 m of testing have shown that no wear is detectable on M50 and Al₂O₃ balls, whereas Ti-6Al-4V pins had already suffered a wear loss of about 1x10⁻⁵ mm³/Nm, Figure 22. Observations at high magnifications showed that the transfer layer consisted mainly of aggregates of fine particles less than 100 nm in size, Figure 23 (c). Thus, the break-in stage prior to reaching the low friction plateau may be related to the time required for the formation of transfer layer.

The results of the lifetime friction tests conducted on DLC-coated 440C substrates under 5 N, 10 N and 20 N load at a velocity of 0.5 m/s are shown in Figure...
It is interesting to note that for long sliding distances, a further reduction in \( f \) occurs after the initial stage until steady-state is reached with friction coefficient down to 0.05-0.07 depending on loading level. Steady-state was reached earlier under the higher loading level as shown in Figure 24.

The slightly higher \( f \) observed during the tests under 20 N is attributed to the larger contact area resulting from the higher loading in agreement with previous reports [157]. A similar trend can also be seen in Figure 22. The observed response indicates that the steady-state stage is attained at much longer sliding distances than the plateau observed in Figure 22 which can be described as an intermediate constant \( f \) stage. The latter stage was also observed in all of the long-duration tests, Figure 24, at about \( 1 \times 10^4 - 2 \times 10^4 \) cycles in agreement with the frictional response shown in Figure 22. The intermediate stage was more pronounced in the tests conducted at the highest loading level (20 N) and lasted from about 8,000 to 30,000 cycles. This can be attributed to more effective transferring of the carbon interlayer to the pin surface under the higher loading.

Furthermore, a long film lifetime was observed in the above experiments, varying from 131 km, 128 km and 90 km for 5 N, 10 N and 20 N contact load, respectively. The average wear rates as a function of loading are given in Figure 24. The overall average of wear rates for these experiments was estimated to be about \( 1.6 \times 10^{-9} \text{ mm}^3/\text{Nm} \) which is significantly lower than that observed at the initial stages of the wear process, Figure 22. In view of the film thickness, the above wear rate can be translated into an ultra-low average penetration rate between 0.0127 and 0.0156 Å/revolution. Thus, if the occurrence of the intermediate stage is mainly due to the formation of the transfer film,
<table>
<thead>
<tr>
<th>Contact Load (N)</th>
<th>Initial Contact Stress (MPa)</th>
<th>Wear Rate ($\times 10^{-9}$ mm$^3$/Nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>720</td>
<td>3.0</td>
</tr>
<tr>
<td>10</td>
<td>910</td>
<td>2.0</td>
</tr>
<tr>
<td>20</td>
<td>1140</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Figure 24 Variation of friction coefficient during tests of 440C balls sliding on DLC-coated 440C discs under 5 N, 10 N and 20 N load (wear-track diameters are 36, 41 and 34 mm, respectively). The arrows indicate the initiation of the steady-state stage (the table above summarizes the initial contact situation and wear parameters in the tests, the numbers next to the arrows indicate the sliding distance in meters).
the long-distance frictional response (Figure 24) suggests that additional changes take place at the contact region that can cause a further reduction in the friction coefficient and wear rate.

2. Characterization of transfer layer and wear debris

The transfer layers extracted from pin surfaces after 1000 m wear testing exhibit similar characteristics. Figure 25 is a TEM micrograph showing a typical microstructure of the transfer layer that was extracted from a Ti-6Al-4V alloy pin surface after 1000 m testing. A fine distribution of particles with a size less than 5 nm (as determined by dark field analysis) is present in the microstructure of the transfer layer. A comparison with the as-deposited microstructure (Figure 21) shows that these particles were formed during wear testing. Electron diffraction analysis shows faint and broader diamond-like diffraction rings ($d = 0.2$ and $0.113$ nm) compared to as-deposited DLC film, evidence of a distorted DLC structure. Furthermore, the halo encircling the central spot with $d = 0.34$ nm corresponding to (00.2) graphite gained intensity and is more evident in comparison to the as-deposited DLC films (Figure 21). These observations suggest that during the initial break-in period significant distortion is produced into the DLC structure (probably due to thermal and/or straining effects) and some DLC starts transforming into graphite. However, a significant part of the transfer layer is still composed of the original but distorted DLC structure. These observations are in good agreement with recent TEM results on post-growth modification of DLC films by laser treatment [89].
Figure 25 TEM micrograph and corresponding diffraction pattern showing the microstructure of the transfer layer containing a fine distribution of graphite nanoparticles. The large arrow indicates the area covered by two "broadened" rings of the diamond-like structure and the smaller arrow indicates the halo corresponding to graphite. (Transfer layer was extracted from a Ti-6Al-4V pin after wear testing against DLC-coated Ti-6Al-4V disc under 10 N load for 1000 m sliding distance).
It was shown that at fluences higher than 100 mJ/cm², graphite nanocrystals with a fine distribution and dimensions from 2 nm to 4 nm were nucleated in the DLC film. Thus, the intermediate stage is more than likely due to formation of transfer layer along with some initial graphitization.

Typical morphology of debris collected from wear track and pin surfaces after 1000 m friction testing is shown in Figure 26(a) [160]. The observed debris morphology is distinctly different from that of the as-deposited DLC. The debris was found to be a discontinuous segregation of clusters of various shapes consisting of agglomerated particles ranging from nano to micro size. The irregular shapes of the clusters are likely the result of friction. A typical diffraction pattern from the clusters is given in Figure 26(b). Mainly, the diffraction pattern consists of a strong diffuse ring at approximately 3.3 Å and three faint rings with d-spacing approximately 2.1 Å, 1.8 Å and 1.2 Å, respectively. The values of 3.3 Å and 1.8 Å are consistent with the (00.2) and (01.2) diffraction of graphite. The d-spacing of 2.1 Å and 1.2 Å is respectively near the d-spacing of (111)_{DLC} and (220)_{DLC} and from their faint and scattered appearance, are considered to evolve from a distorted DLC film structure.

The observed characteristics of the diffraction pattern from debris suggests that during sliding, as-deposited film is significantly distorted and most of DLC transforms into graphite. The resulting debris is the mixture of distorted DLC and graphite. This aspect was further evidenced by dark field analysis. Figures 27(a) and (b) show respectively, bright and dark field images of a section of a transfer layer. The dark field was obtained by utilizing part of the (00.2) diffraction ring. It is evident that small graphite particles (about 5-10 Å in diameter) are present, Figure 27(b). There is a
Figure 26  (a) High magnification bright field TEM micrographs of wear debris after 1000 m friction test, (b) the diffraction pattern from the wear debris.
Figure 27 (a) Bright field image of a portion of the transfer layer, (b) dark field image of the same area using part of the (00.2) diffraction ring.
(c) high magnification of an area in (a) showing orientation arrangement of nucleated graphite particles along the sliding direction.
characteristic noted that the graphite forms in streak-like clusters along the sliding direction. This particular cluster formation suggests that friction related effects (heat and strain) contribute to the transformation of DLC into graphite. The orientation arrangement of the nucleated graphite particles is evident at high magnification observations, Figure 27(c).

The first order Raman spectrum for graphite consists of a single line at 1580 cm⁻¹ (G peak) but in disordered graphite, another broad line appears at ~1355 cm⁻¹ (D peak). It has been shown by previous studies that typical DLC Raman spectra are composed of two main peaks at ~1540 cm⁻¹ and ~1360 cm⁻¹ [161]. The high frequency band in DLC Raman spectra has been assigned to the graphite-like sp²-bonded carbon and the low frequency band to the sp²-bonded phase (and any probable contributions from the graphite-like D band) [162].

Figure 28 illustrates typical laser Raman spectra obtained from the as-deposited DLC film and from the wear track region after wear testing (10 N load, 1000 m). The spectra were deconvoluted using two Gauss functions, where a linear background was subtracted. The parameters of the Gaussian line shape analysis for the spectra are summarized in Table 6. It is evident that the high frequency peak (G) in the spectrum taken from the wear track has been shifted to higher frequency and coincides with that expected from graphite. Also, there is a significant increase in the intensity of the low frequency peak due to D band contributed from disordered graphite. The Raman spectra clearly show a change in the structure of the wear track surface region from diamond-like to graphite-like.

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Figure 28  Typical Raman spectra taken from (a) as-deposited DLC film and (b) wear track region after testing.
Table 6  Characteristic parameters of Gaussian line shape analysis of Raman spectra from as-deposited DLC films and wear track region after wear testing. The number in parentheses show the 95% confidence level errors.

<table>
<thead>
<tr>
<th>DLC Film</th>
<th>v_D Position cm⁻¹</th>
<th>Γ_D FWHM cm⁻¹</th>
<th>I_D Intensity a.u.</th>
<th>v_G Position cm⁻¹</th>
<th>Γ_G FWHM cm⁻¹</th>
<th>I_G Intensity a.u.</th>
<th>I_D/I_G</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-Deposited</td>
<td>1383(45)</td>
<td>393(30)</td>
<td>100699</td>
<td>1545(8)</td>
<td>150(15)</td>
<td>54508</td>
<td>1.83</td>
</tr>
<tr>
<td>Wear Track</td>
<td>1391(18)</td>
<td>370(18)</td>
<td>154773</td>
<td>1580(4)</td>
<td>105(7)</td>
<td>55443</td>
<td>2.8</td>
</tr>
</tbody>
</table>
3. Graphitization of DLC and friction mechanism

As deposited DLC is thought to be a metastable structure and it tends to transform into graphite after an energy barrier is overcome. The present observations demonstrate that the process of sliding friction provides the energy required for the transformation of DLC (diamond cubic) to graphite (hexagonal). Previous studies showed that the $sp^3$ carbon structure can be converted to pure $sp^2$ structure by heating at about 500°C to 600°C [163]. The internal energy change per unit volume accompanying this process is

$$ Q = C_{DLC} \rho \Delta T, \quad (10) $$

where $C_{DLC}$ is the specific heat of DLC (about 600 J/kg K), $\rho$ is its density (2600 kg/m$^3$) and $\Delta T$ is the temperature rise at which the $sp^3$ structure is converted into $sp^2$ structure. From the above data, $Q$ is calculated to be between $7.4 \times 10^8$ J/m$^3$ and $9 \times 10^8$ J/m$^3$. The calculated energy range can be considered as an upper limit of the activation energy for the transformation.

The real contact area during friction is determined by the micro-topography of the surfaces. According to Hertzian contact theory, the radius $a$ of the equivalent circular contact area is a function of the external load $P$, the diameter of the pin $D$, the elastic modulii of the materials in contact ($E_{pin}$ and $E_{DLC}$) and their Possion’s ratios ($\nu_{pin}$ and $\nu_{DLC}$), Appendix 1. The calculated values of the radius $a$ of the initial contact area for the systems involved in the present study are listed in Table 7.
Table 7  The calculation of temperature rise during friction.

<table>
<thead>
<tr>
<th>Pin on Disc</th>
<th>$a$ (µm)</th>
<th>$K_{pin}$ (W/mK)</th>
<th>$K_{DLC}$ (W/mK)</th>
<th>$f_{init}$</th>
<th>$ΔT$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>M50 on DLC</td>
<td>2.88</td>
<td>21.6</td>
<td>0.7-7.0</td>
<td>0.20</td>
<td>310-389</td>
</tr>
<tr>
<td>Ti-6Al-4V on DLC</td>
<td>5.35</td>
<td>7.2</td>
<td>0.7-7.0</td>
<td>0.18</td>
<td>306-532</td>
</tr>
<tr>
<td>Al_2O_3 on DLC</td>
<td>2.74</td>
<td>0.5</td>
<td>0.7-7.0</td>
<td>0.12</td>
<td>730-4562</td>
</tr>
</tbody>
</table>

The calculations are based on the following data:
Elastic modulus: $E_{M50} = 207$ GPa, $E_{Ti-6Al-4V} = 113.7$ GPa, $E_{Al_2O_3} = 343$ GPa, $E_{DLC} = 350$ GPa;
Poisson’s ratio: $ν_{M50} = 0.31$, $ν_{Ti-6Al-4V} = 0.321$, $ν_{Al_2O_3} = 0.25$, $ν_{DLC} = 0.3$;
Pin diameter: $D_{M50} = 0.0095$ m, $D_{Ti-6Al-4V} = 0.254$ m, $D_{Al_2O_3} = 0.0095$ m;
Frictional parameters: $P = 10$ N, $ν = 0.05$ m/s.
The work due to friction at the contact area per rotating cycle can be estimated by

\[ W = P f_{in} (2a), \]  

(11)

where \( f_{in} \) is the initial friction coefficient. Using the parameters shown in Table 7, the values of \( W \) ranged from \( 6.6 \times 10^{-6} \) J to \( 1.9 \times 10^{-5} \) J. Also, assuming a perpendicular cylinder beneath the contact asperity going through the thickness of the DLC film, the required energy for graphitization, \( E \), of a depth, \( d \), of this cylindrical volume can be given by

\[ E = \pi a^2 d Q, \]  

(12)

Using the data in Table 7, it can be estimated that \( E \) varies from \( 7.0 \times 10^{-9} \) to \( 3.2 \times 10^{-8} \) J. Thus, comparing values of \( W \) and \( E \) it can be seen that for the present study, the energy produced by friction across the contact area is in principle sufficient to transform the whole thickness of the DLC film under the contact area into graphite. However, the extent of graphitization will depend on the transformation kinetics which is related to the resulting rate of dissipation and accumulation of friction-induced energy beneath the contact region, i.e. the temperature rise.

On the basis of a simple model for flash temperature (\( \Delta T \)) at asperities due to friction [60], an approximate value of \( \Delta T \) can be obtained by applying equation 7. For the present system, \( K_{pin} \) and \( K_{DLC} \) are the values of thermal conductivity of the pin material and DLC (\( J = 1 \) in this case). The calculated values of \( \Delta T \) are shown in Table 7.

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The thermal conductivity of DLC films varies depending on film composition and structure. A range in the thermal conductivity of the DLC films was assumed based on values from the literature [164]. It is important to note that for all cases, and regardless of the pin material, the calculations indicate that the expected minimum temperature rise on the local asperity contact during one wear cycle is above 300° C. These values are in general agreement with previous flash temperature calculations [165]. It should be noted that the flash temperatures at the "hot spots" produced by friction are expected to have a short duration [61]. Hot spots are expected to be cooled down during the time interval between subsequent contacts and due to heat losses by conduction and radiation. On the other hand, repeated friction is expected to continuously supply heat to the contacting asperities. Considering the above factors, a heat balance indicates that under these conditions the overall temperature will not increase significantly (5-10° C). Thus, only the flash temperature at the contact asperities can be considered as the critical energy source to trigger the transformation of DLC into graphite.

The above conclusion is also consistent with the experimental evidence. The particular pattern exhibited by the graphite particles formed during wear (Figure 27), indicates that nucleation of graphite occurred locally at asperity contacts where high flash temperatures may have be developed [160]. The TEM observations show that the graphite streaks extending for about 0.2-1 μm in length and the individual graphite nuclei are a few nm in size. The observed small graphite particle size (nucleus) suggests that temperatures higher than the transformation temperature lasted for a short period of time and their occurrence can be attributed to flash temperature at asperity contact. If the observed length of the graphite streak is taken as a rough measure of the contact area at
individual asperities, then based on equation 7 the flash temperature is estimated to be much higher than 600°C and is consistent with the previous argument.

In addition, the experimental observations [Figures 23 and 25] show that during friction, a carbon-rich transfer layer forms on the pin surface. Since the transfer layer is mainly composed of DLC, the contact is modified from that of metal/DLC (in the case of metallic pin) to that of DLC/DLC and significant temperature rise may result at the contact due to the lower thermal conductivity of DLC. Differential scanning calorimetry experiments have shown that release of hydrogen atoms from the DLC structure occurs at about 450°C [163]. Also, thermal annealing experiments [166] on IBD DLC films showed that hydrogen begins to evolve at about 300°C while the $sp^2$ fraction starts at 400°C. It is believed that hydrogen atoms, introduced by the deposition process, play a critical role in promoting and stabilizing $sp^2$ tetrahedral bonds in the DLC structure [78]. It is also suggested that several hydrogen atoms are compressed into one vacancy of aromatic domain in the DLC lattice [93], distorting the diamond cubic lattice.

In the present research, the lattice parameter of DLC is found to be 3.64 Å, which is somewhat larger than that of real diamond (3.57 Å). During wear, a friction-induced annealing process is expected to be probably able to result in gradual hydrogen atom liberation from the DLC structure and reduction of the DLC lattice distortion in aromatic domains. The $(111)_{\text{DLC}}$ plane of diamond cubic structure and $(00.2)_{\text{GR}}$ graphite (hexagonal) plane have identical atomic arrangements and a small difference in the atomic spacing, 2.57 Å for $(111)_{\text{DLC}}$ and 2.46 Å for $(00.2)_{\text{GR}}$. After hydrogen is released from the DLC structure, the extent of the $sp^2$ C-H bonding is reduced, resulting in $sp^2$ covalent bonding causing a decrease in the $(111)_{\text{DLC}}$ interplanar distance and atomic...
spacing, which makes the (111)\text{DLC} more coherent to (00.2)\text{GR}. Thus, releasing hydrogen atoms from the DLC structure provides the prerequisite for the transformation of DLC structure to graphite lattice. This seems to be supported by the ED patterns indicating that the formed graphite has a strong (00.2) nucleation preference and by the particular orientation arrangement of the graphite particles, Figures 26(b) and 27(b).

It should be noted that the transformation of DLC to graphite may also be facilitated by the shear stresses existing in the surface layer. The friction-induced shear forces cause strain parallel to the contacting surfaces. This strain energy produced by friction can be used to accomplish the necessary deformation for the transformation of DLC structure to graphite after the release of hydrogen atoms. The stacking of (111)\text{DLC} and (00.2)\text{GR} planes are in an ABCABC... and ABAB... sequence, respectively. If layer C slides across layer B, the layer C tends to coincide with layer A and the stacking sequence becomes ABAB.... As discussed above, after the release of hydrogen atoms from the DLC structure, the (111)\text{DLC} and (00.2)\text{GR} become coherent and the shearing on the (111)\text{DLC} plane probably produces a hexagonal layer by changing the stacking sequence of atoms on the layer. Under these conditions wear-induced graphitization is expected to result in microcrystalline graphite with graphite layers stacked in an arbitrary sequence and orientation.

In view of the graphitization process discussed above, the initial reduction in the friction coefficient observed during the break-in stage of the tribological experiments can be attributed to the gradual release of hydrogen atoms from the \text{sp}^3 structure producing a low-shear strength structure. The intermediate constant friction plateau can be related to the formation of the transfer layer, and small-scale graphitization at "hot spots". The low
friction in steady-state stage can be related to the extensive graphitization in the tribolayer. The low shear strength between hexagonal planes in graphite (due to weak Van der Waals forces) can account for the low friction coefficient and ultra-low wear rate (less than 1.6 x 10^{-9} mm³/Nm equivalent to about one carbon monolayer per 100-200 cycles) observed in this stage [156]. This suggests that the graphitized tribolayer between the two surfaces in contact is composed of low-strength atomic carbon interlayers that can undergo repeated shear. The present results are in agreement with previous observations of carbon-rich transfer layer formation on steel and Si₃N₄ ball surfaces rubbed against DLC films and the associated low friction coefficients [157].

The proposed wear mechanism is consistent with the existing phenomenology of DLC tribology and with the present experimental results. According to the proposed wear-induced graphitization mechanism, temperature rise (flash temperature) and shear deformation due to frictional energy are the two primary components of this process. The wear and environmental parameters which are closely related to these two effects are considered to be sliding velocity, loading level, humidity (will affect heat dissipation and hydrogen release) and temperature. Thus, in the following sections wear tests are conducted at different loading levels, sliding velocities, values of humidity and temperatures in order to assess the effect of these parameters on the tribological behavior and graphitization process and provide further insight into the proposed mechanism.
4. The effect of operational parameters on the tribological behavior of DLC film

Table 8 summarizes the testing parameters and experimental results of the tribological behavior of ZrO$_2$/DLC-coated SiC [167]. More specifically, the parameters shown are the initial Hertzian stress ($\sigma_h$), the initial and steady-state friction coefficient ($f_i$ and $f_{ss}$, respectively), the sliding distance to reach steady-state ($S$) and the wear rate of ball ($W_B$) and disc ($W_D$) material. It is noted that in agreement with previous results [26, 156], the DLC films exhibited low friction and ultra-low wear rates. Also, it is evident that sliding velocity and loading level exercise significant effects on the tribological behavior of DLC films.

The TEM observations and ED analysis of debris collected from wear scars after testing showed that all wear debris was mainly composed of graphite except for debris from the tests conducted under low velocity (0.06 m/s) and low loading level (1 N), Test 1. Figures 29 (a) and (b) show typical morphology and microstructure of the debris. The corresponding diffraction pattern analysis of the wear debris showed mainly the (00.2)$_{GR}$ $sp^2$-graphite reflection ($d \approx 3.4$ Å), Figure 29 (c), confirming the presence of graphite in agreement with the previous studies [155, 159]. Dark field analysis showed that the graphite particles had a size of about 3 - 4 nm and exhibited an orientation pattern, more than likely coinciding with the sliding direction, Figure 29 (d). These and the observations made earlier in the present study regarding the microstructure of the graphitized layer [160], show that after nucleation, there is limited growth in the graphite particles which maintain a relatively small size (~ 4 nm). According to the proposed mechanism, the observed low friction can be attributed to the low shear strength between
Table 8  Tribological parameters for the tests of ZrO$_2$/DLC-coated SiC.

<table>
<thead>
<tr>
<th>Test No</th>
<th>Velocity $u$, (m/s)</th>
<th>Load $F$, (N)</th>
<th>$\sigma_H$, (MPa)</th>
<th>$f_{in}$</th>
<th>$f_{ss}$</th>
<th>$S$, (m)</th>
<th>$W_B^-$, ($\times 10^{-9}$ mm$^3$ m$^{-1}$N$^{-1}$)</th>
<th>$W_P^-$, ($\times 10^{-7}$ mm$^3$ m$^{-1}$N$^{-1}$)</th>
<th>$R$, $(\times 10^4$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.06</td>
<td>1</td>
<td>395</td>
<td>0.18</td>
<td>0.18</td>
<td>---*</td>
<td>10.1</td>
<td>ND</td>
<td>---</td>
</tr>
<tr>
<td>2</td>
<td>1.6</td>
<td>1</td>
<td>395</td>
<td>0.10</td>
<td>0.06</td>
<td>8000</td>
<td>3.56</td>
<td>8.36</td>
<td>2</td>
</tr>
<tr>
<td>3</td>
<td>0.1</td>
<td>10</td>
<td>851</td>
<td>0.13</td>
<td>0.08</td>
<td>9500</td>
<td>1.82</td>
<td>2.48</td>
<td>0.1</td>
</tr>
<tr>
<td>4</td>
<td>1.6</td>
<td>10</td>
<td>851</td>
<td>0.08</td>
<td>0.05</td>
<td>4300</td>
<td>0.566</td>
<td>1.99</td>
<td>3.7</td>
</tr>
</tbody>
</table>

$\sigma_H$ = initial Hertzian contact pressure, $f_{in}$ = initial friction coefficient, $f_{ss}$ = steady-state friction coefficient, $S$ = sliding distance required to reach steady-state, ND = nondetectable, $R$ = rate for graphitization. * Steady-state was not reached under these conditions for a sliding distance of 25 km.
Figure 29  TEM micrograph showing (a) typical debris morphology, (b) microstructure of debris where graphite particles can be seen.
(c) the corresponding diffraction pattern showing mainly the (00.2) graphite reflection, (d) the dark field image of the wear debris.

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the hexagonal planes in graphite. Under these conditions, the wear process can be envisioned as a low-rate continuous generation and consumption of the graphitized tribofilm.

Thus, the relatively higher friction coefficient ($f = 0.18$) in Test 1 is attributed to the friction between DLC (rather than graphite) and the ZrO$_2$ ball. The friction coefficient in the rest of the tests reached a low steady-state value ($f < 0.08$) due to the presence of graphite as confirmed by TEM. The higher wear rate of the ball material during Test 1 is consistent with the higher $f$ and the presence of DLC that has a higher hardness than graphite. Also, the absence of graphite from the wear track in Test 1 shows that below certain limiting conditions (a combination of low sliding velocity and loading level), the transformation requirements for graphitization are not met even after 10 km sliding distance. In an effort to explore this aspect a little further, an additional experiment was conducted under the same wear parameters for a sliding distance of 25 km. Again no steady-state friction was reached.

A comparison among Tests 2, 3 and 4 shows that both sliding velocity and loading level have a significant influence on the graphitization process. Utilizing the sliding distance $S$ to reach steady-state (graphitization) as a criterion and for the present experimental parameters, the results show that sliding velocity has a greater effect than loading level. According to the wear-induced graphitization mechanism discussed in the last section, reduction in the friction coefficient $f$ during wear involves the gradual releasing of hydrogen atoms from $sp^3$ domains at "hot spots" and shearing of the weakened hydrogen depleted DLC layer producing graphite. Sliding velocity (contact frequency) is expected to have a greater impact in increasing temperature at asperity
contacts than loading level. Indeed, predictions of friction-induced temperature rise show that the flash temperature at contacting regions is proportional to sliding velocity and applied load, but inversely proportional to the contact area (Equation (7)). Since an increase in the applied load results in an analogous larger contact area, sliding velocity is expected to be more effective in increasing temperature at asperity contacts than loading level and thus facilitating the precursor H release stage of the graphitization process. On the other hand, low rotational frequency results in a lower transfer rate of friction energy, a long time interval between subsequent contact events, allowing heat transfer and thus, reducing asperity temperature. However, the results suggest that under a sufficiently high applied load, graphitization can occur at a low sliding velocity, but after extensive total sliding distance (Test 3).

In order to describe the rate of formation of the low friction graphitized tribolayer under the various loading and sliding velocity values, a parameter, \( R \), was estimated and its value for the various wear tests is shown in Table 8. The parameter is simply calculated from the time required to reach steady-state (graphitization) and is an indicator of the formation rate of the low-friction graphitized tribolayer. For example, a comparison in \( R \) between Tests 3 and 4 (a 16 time increase in velocity causes a 37 times increase in \( R \)) and Tests 2 and 4 (a 2.15 times increase in \( \sigma_r \) causes a 1.85 times increase in \( R \)) indicates again that sliding velocity exercises a greater effect than applied load.

As mentioned in the previous section, the two primary requirements of the proposed wear-induced graphitization mechanism are H release caused mainly at “hot spots” by friction and shearing of the produced low-strength layer. The wear parameters closely relating to these two processes are considered to be sliding velocity and loading.
level. Furthermore, the present results suggest that these two parameters have a
significant effect on the graphitization process. Thus, assuming that the graphitization
rate (formation of a graphitized tribolayer) is mainly a function of these two parameters,
\( R \) can be described as

\[
R = C \, v^{\alpha} \sigma^{\beta}
\]  

(13)

where \( v \) is the sliding velocity (m/s), \( \sigma \) the applied Hertzian stress (MPa), \( \alpha \) and \( \beta \)
power coefficients and \( C \) a rate constant. Based on the experimental data in Table 8
together with the information in Figure 24 and as a first approximation taking the value
of \( \sigma_{\text{ap}} \) as the applied stress, the values of the coefficients involved in the above equation
were estimated using regression analysis. The results showed that \( C \approx 4.54 \times 10^{-7} \, \text{s}^{0.3} \, \text{m}^{-1.5} \, \text{MPa}^{0.876} \), \( \alpha \approx 1.30 \) and \( \beta \approx 0.876 \). Using the wear parameters during Test 1 (0.06 m/s
and 395 MPa), it is predicted that graphitization will occur after a sliding distance of
more than 28 km which is consistent with the experimental results.

5. The influence of environmental parameters on the tribological behavior of
DLC films

It is important to note that the proposed wear-induced graphitization mechanism
involving the formation of a low friction graphitized tribolayer is consistent with the
existing phenomenology of DLC tribology. For example, an important issue has been
the effect of humidity on the DLC tribological response. DLC films are considered
moisture-sensitive and in general, their friction coefficient increases with increasing
humidity [20]. Recent tribological experiments by Jia, et al [168] showed that wear of
DLC in humid air (40% humidity) is larger than that in dry air. Also, the friction coefficient in humid air is initially higher than that in dry air, but the steady-state friction coefficient is the same (~ 0.05) for both cases. These results are consistent with the wear-induced graphitization mechanism since the presence of a thin condensation layer of moisture at the asperity contact is expected to reduce the flash temperature and produce a slower formation rate (smaller value of $R$) of the graphitized tribolayer.

Additional friction experiments were performed in order to obtain further information of the effect of environmental humidity and temperature on the tribological behavior of DLC coating and test the wear-induced graphitization model [169]. Table 9 summarizes the frictional tests in various environments, and Figure 30 presents the variation of the friction coefficient with sliding distance of DLC-coated SiC substrate for the various experimental conditions.

The influence of humidity on the tribological behavior can be deduced by comparing tests 1, 2 and 3. Test 1 was conducted at normal laboratory environment (humidity ~40%) which represents ordinary application environment for DLC films. This test produced low wear of pin and disc, $0.66 \times 10^{-9}$ mm$^3$ m$^{-1}$ N$^{-1}$ and $0.8 \times 10^{-7}$ mm$^3$ m$^{-1}$ N$^{-1}$, respectively. The coefficient of friction had a relatively higher initial value and a very low value at steady-state ($f_s = 0.075$).

The observed low friction coefficient in test 1 can be attributed to the formation of graphitized tribolayer between the pin and disc materials, and as a result, the low shear strength between hexagonal planes in the graphite structure. Under this condition, after the steady-state stage is reached, the wear process can be envisioned as a low-rate continuous consumption and generation of graphitized tribofilm, as discussed before.
Table 9. Summary of Friction Tests of ZrO$_2$ on DLC-Coated SiC Substrate

<table>
<thead>
<tr>
<th>Test No</th>
<th>Velocity $v$, (m/s)</th>
<th>Load $P$, (N)</th>
<th>$T$, (°C)</th>
<th>Humidity, (%)</th>
<th>$\sigma_H$, (MPa)</th>
<th>$f_m$</th>
<th>$f_s$,</th>
<th>$S$, (km)</th>
<th>$W_b^*$, ($x10^{-9}$ mm$^3$ m$^{-1}$ N$^{-1}$)</th>
<th>$W_d^*$, ($x10^{-9}$ mm$^3$ m$^{-1}$ N$^{-1}$)</th>
<th>$R$, ($x10^4$ s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>10</td>
<td>25</td>
<td>40</td>
<td>851</td>
<td>0.16</td>
<td>0.075</td>
<td>40</td>
<td>0.66</td>
<td>0.80</td>
<td>0.13</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>10</td>
<td>25</td>
<td>0</td>
<td>851</td>
<td>0.07</td>
<td>0.02</td>
<td>1.97</td>
<td>0.68</td>
<td>0.63</td>
<td>2.53</td>
</tr>
<tr>
<td>3</td>
<td>0.5</td>
<td>10</td>
<td>25</td>
<td>100</td>
<td>851</td>
<td>0.10</td>
<td>0.10</td>
<td>NG</td>
<td>1.12</td>
<td>1.05</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>0.06</td>
<td>10</td>
<td>-10</td>
<td>40</td>
<td>851</td>
<td>0.15</td>
<td>0.30</td>
<td>NG</td>
<td>60.3</td>
<td>4.89/(3.5 km)*</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0.5</td>
<td>5</td>
<td>200</td>
<td>40</td>
<td>675</td>
<td>0.04</td>
<td>0.025</td>
<td>0.02</td>
<td>1.1</td>
<td>0.707</td>
<td>250</td>
</tr>
</tbody>
</table>

$\sigma_H$ = initial Hertzian stress, $f_m$ and $f_s$ = initial and steady-state coefficient of friction, respectively, $S$ = sliding distance before reaching steady-state stage, $W_b^*$ and $W_d^*$ = wear rate of ball and disc, respectively, $R$ = graphitization rate (inverse of time required to reach graphitization), NG = no graphitization occurred;

* The number in parenthesis indicates the distance at which the film was worn out.
Figure 30. Variation of friction coefficient with sliding distance of DLC-coated SiC substrate under various environmental conditions (The small graph indicates the friction behavior during initial 100 m sliding distance in Test 5.)
The extensive sliding distance (40 km) required before reaching low friction steady-state indicates a very low graphitization rate under this humidity level. This behavior can be also represented by a low value of graphitization rate, $R = 0.13$, (reciprocal of the time required to reach the low friction steady-state stage).

Test 2 was performed in dry air (0% humidity). The experimental results show very low $f$ values at steady-state ($f_s = 0.02$), low values of $S$ (1.97 km), and wear rate of pin and DLC film are all consistent with enhanced graphitization occurring during friction. The very low wear volume of DLC film and the corresponding high calculated graphitization rate, $R (2.53, \text{almost 20 times that of test 1})$ are equitable with very short sliding distance (1.97 km) to reach steady-state. The low wear rates of pin and DLC-coated disc can very reasonably be attributed to the low friction coefficient in large portion of the friction process.

In the high humidity environment (test 3, 100% humidity), the friction process can be described by constant friction coefficient. The relatively high values of $W_D'$ and $W_J'$ are attributed to the direct contact between the pin material and the hard DLC film rather than between the pin and a soft tribolayer in the wear track. Also, the continuous high friction coefficient ($f_m \approx f_s = 0.10$) suggests that no significant graphitization occurred during friction under such a high humidity environment.

From the analysis of tests 1, 2 and 3, it can be seen that humidity of environment exercises a significant influence on the graphitization process of DLC film. Humidity can affect the friction process by forming a moisture layer at the pin/disc contact interface. According to the wear-induced graphitization mechanism of DLC proposed in this research, the transformation is advanced with hydrogen atom release from DLC structure.

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during the break-in stage. Thus, the moisture layer on DLC surface produced by the adsorbed water molecules in high humidity environment can essentially block the release of hydrogen atoms from the DLC structure and consequently decelerate or even completely stop the graphitization process. In addition, the water vapor from the high humidity environment can condense on the contact area and may promote the detachment of the loose tribolayer formed during friction. This can result in a continuous direct contact between the pin and disc materials, and thus result in a high friction coefficient and wear rate, as found in test 3.

Furthermore, according to the wear-induced graphitization mechanism, a condensed water layer at asperity contacts can have a cooling effect on microsize “hot spots” and thus significantly reduce friction-induced thermal effects. Consequently, high enough flash temperatures may not be attained and the graphitization kinetics are expected to be suppressed.

In an extremely low humidity environment (0%, test 2), the observed low friction coefficient, low wear rates of both pin and DLC film and high graphitization rate show that a dry environment promotes the graphitization process. The present results show that by increasing the humidity level, the coverage of asperity contacts by water molecules decelerates the graphitization process. In the very high humidity environment (100%, test 3), no graphitization was observed and a relatively high value of $f$ is maintained. Previous studies showed that in humid air, the surface of DLC coating can be oxidized by a tribochemical reaction forming a C=O bond which caused an increase in the friction coefficient [24]. Other studies have also reported an increase of friction with humidity or decrease of friction under dry nitrogen environment [110-112].
The significance of temperature on the tribological behavior of the DLC film can be found by comparing tests 1, 4 and 5. It is interesting to note that at -10°C, the DLC film was worn out after a short sliding distance (3.5 km), accompanied by a sudden increase in the friction coefficient, Figure 30. This phenomenon resulted in very high wear rates of pin and disc materials (60.3 x 10^-9 mm^3 m^-1 N^-1 and 4.89 x 10^-7 mm^3 m^-1 N^-1, respectively), compared with the corresponding data for test 1. It is important to note that in previous section (Table 8), wear testing under similar conditions as those of test 4 but at room temperature, caused graphitization.

The results of the friction test conducted at 200°C (test 5) are shown in Figure 30. This test showed compatible wear rates of pin and disc (1.1 x 10^-9 mm^3 m^-1 N^-1 and 0.707 x 10^-7 mm^3 m^-1 N^-1, respectively) with those of test 1, but extremely high graphitization rate (250 s^-1). It is evident that under the higher testing temperature the hydrogen release rate is accelerated significantly promoting the graphitization process. It is interesting to note that graphitization in this test occurred very fast within the first 23 m of testing (insert in Figure 30). Careful observation of the pin surface after wear testing revealed a much higher volume of black loose particles formed during the friction process, compared with the other tests under the same total sliding distance. This result demonstrates that high environmental temperature can accelerate the graphitization process (after only about 20 m sliding distance). Another interesting event occurring in test 5 is that after a short very low friction steady-state stage (f = 0.025), the coefficient of friction increased gradually, Figure 30, but still remained at low levels (f < 0.07). This behavior is more than likely due to structure softening of the DLC film produced by the extensive graphitization that gradually results in a thick graphitized layer that is soft and...
increases the area of contact. This further indicates that environmental temperature plays a key role in the tribological behavior and low temperatures can prevent graphitization of the DLC coating.

The influence of environment temperature on the tribological behavior of DLC film is consistent with and further validates the proposed wear-induced graphitization mechanism. At low temperatures (or in the presence of humidity), the friction-induced “hot spots” are expected to be cooled down due to the heat loss by conduction and convection during the time interval between two subsequent contacts. The escaping of hydrogen atoms from the DLC structure is actually based on the heat accumulation in large number of micro-size contacts. The low temperature of the environment can accelerate the heat transfer process by increasing conduction and convection between local “hot spots” and the environment. The continuous heat loss by conduction and convection from friction-induced “hot spots” restricts the release of hydrogen atoms from the DLC structure and the subsequent formation of low shear strength tribolayer. The direct contact between the hard DLC film and pin for long distance during friction produced high wear rate of pin and disc materials, as indicated by test 4. On the contrary at high temperatures the hydrogen release rate is accelerated promoting graphitization.

C. FE Analysis of the Yielding Behavior of a Hard Coating/Substrate System with Graded Interface Under Indentation and Friction

FE modeling was conducted in this part of the research to provide the theoretical background on the stress distribution and yielding process in coating/substrate system.
Also, the information based on the theoretical predictions served as a guide for the experimental studies.

1. Establishment of FE model

Consider a hard coating bonded perfectly to a semi-infinite body of the substrate so that the combination of coating and substrate can be assumed to be a single bulk medium. A rigid surface, assumed to be an infinitely long circular cylinder, is indented into the coating and is represented by an undeformable circular arc that is tangent with the half-space at the center-point, with a radius of 10 µm. This value of the contact radius is reasonable for textured asperities of counterface and wear particles. During indentation of the pin on the flat coated surface, the semi-infinite body is in the condition of plane strain. The indentation condition and corresponding coordination system are shown in Figure 31.

The distribution of normal contact traction, \( N(x) \), on the contact area is assumed to be of the elliptical form within the contact width, \( 2a \), of the contact region [170]:

\[
N(x) = \frac{2P}{\pi a} \sqrt{1 - \frac{x^2}{a^2}} \quad (\text{for } |x| = a),
\]

where \( P \) is the normal load per unit length of cylindrical indenter. The value of \( a \) can be obtained using the method given in Appendix 2. This load was applied to the FE model in a piecewise stepped surface force normal to the face of each element to approximate the analytical expression. The tangential traction due to friction, \( F(x) \), along the contact width is accordingly calculated by:
Figure 31  FE model and coordinate system for indentation and friction.
\[ F(x) = fN(x) \quad \text{(for } |x| = a), \]

where \( f \) is the coefficient of friction. This load is applied as a surface traction using the stepped approximation of \( N(x) \).

A Cartesian coordinate system \((o, x, z)\) is centered on the coating/substrate interface. The material dimensions included in the FEM analysis depend on the value of \( a \). It has been shown previously that the effect of loading on the contact area becomes insignificant at a horizontal distance of approximately 4 to 6 times the contact width of the indentation and a vertical distance approximately 4 to 10 times the contact width of the indentation [171]. In this analysis, the horizontal and vertical distances are all chosen to be about \( 8a \) and it is assumed that the displacements \((U_x, U_y)\) of each nodal point located on the defined boundary are constrained to zero. An array of 1700 to 1800 two-dimensional 8-node isoparametric quadrilateral elements was utilized to model the semi-infinite medium. To obtain accurate stress distributions on the contact area and highly stressed zone near the contact area, the finite element mesh of the half-space was refined in this region. The horizontal and vertical dimensions of the mesh beneath the contact region are 0.05\( a \) and 0.33\( t \) (\( t \) is the thickness of the coating), respectively. The multifunction finite element program ANSYS(5.0a) was used for calculation and processing of the results.

2. Evaluation of the finite element model

To evaluate the accuracy of the finite element model, a system was assumed composed of a steel pin and Ti-6Al-4V alloy substrate without coating and tested for \( P = \)
50,000 N/m and \( f = 0 \) and 0.5. The results calculated by FEM were compared with analytical ones of stress distribution along the \( z \) axis (\( x = 0 \)) given in reference [172]. The results from both approaches are presented in Figures 32(a) and (b), where a reasonably good agreement is shown for the FE model. The main difference between analytical and FEM solutions is due to the mesh refinement in the high stress gradient zones. This refinement is limited by the allowable problem size in the software.

The analysis of equivalent stress contours corresponding to the cases of \( f = 0 \) and \( f = 0.5 \) reveals that pure normal traction results in the symmetric distribution of the equivalent stress, while addition of tangential traction, due to friction, distorts the distribution of equivalent stress to the friction direction. This behavior has been previously demonstrated [135].

3. Yielding criterion and properties of the graded layer

For the system considered in the present study, failure of the hard coating occurs due to local plastic flow in the subsurface region of the substrate. According to the elasto-plastic theory in isotropic materials, elastic deformation ceases and yielding commences when the von Mises yield criterion is satisfied, i.e.:

\[
\sigma_m = \left\{ \frac{1}{2} \left[ (\sigma_1 - \sigma_2)^2 + (\sigma_2 - \sigma_3)^2 + (\sigma_3 - \sigma_1)^2 \right] \right\}^{1/2} \geq \sigma_y
\]

(16)

where \( \sigma_m \) is the von Mises equivalent stress, \( \sigma_1, \sigma_2 \) and \( \sigma_3 \) are the first, second and third principal stresses, respectively, and \( \sigma_y \) is the local yield strength.
Figure 32 Comparison between analytical and calculated solutions for (a) $f = 0$ and (b) $f = 0.5$. 

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In this study, the nitrided substrate possesses a gradient in yield strength. Based on previous investigations, the yield strength in tension of an isotropically deforming material can be considered to be one-third of the indentation hardness when the strain-hardening coefficient is negligibly small. In the present analysis, the measured hardness of DLC films (30 GPa) [156] and hardness profile determined in the nitrided layer [39] are used to derive the yield strength profile of the coating and graded interface, respectively. The hardness profile of nitrided Ti-6Al-4V and the corresponding yield strength profile are shown in Figure 33.

The mechanical properties of the materials used in the model are listed in Table 10. The elastic modulus of bulk (unprocessed) Ti-6Al-4V alloy can be considered to be that of the nitrided Ti-6Al-4V layer since the low percentage of nitrogen atoms in the layer (<10%) will not create a noticeable variation in $E$.

In the present analysis, the radius of contact ($R$), the half width of the contact ($a$) and the contact stress ($P_0 = 2P/\pi a$), were used to normalize the coating thickness ($t$), distance from the coating/substrate interface ($z$), and the calculated equivalent stress values, respectively.

4. Analysis, results and discussion

Spatial equivalent stress distribution and yielding zone Figure 34 presents the distribution of von Mises equivalent stress at various depths under the combination of normal and tangential tractions for a system composed of a low friction hard coating (DLC with $f = 0.1$) on a soft substrate (Ti-6Al-4V alloy). The curves show peak values of equivalent stress passing very near the center-line of the contact region ($x = 0$). A
Table 10  Elastic modulus and Poisson’s ratio of coating and substrate materials.

<table>
<thead>
<tr>
<th></th>
<th>$E$ (GPa)</th>
<th>$\nu$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Indenter (steel)</td>
<td>207</td>
<td>0.31</td>
</tr>
<tr>
<td>Coating (DLC) [177]</td>
<td>213</td>
<td>0.3</td>
</tr>
<tr>
<td>Substrate (Ti-6Al-4V)</td>
<td>113.7</td>
<td>0.321</td>
</tr>
</tbody>
</table>

Figure 33  Hardness and yield strength profiles for nitrided Ti-6Al-4V alloy.
Figure 34  Distribution of equivalent stress at various depths in the substrate ($\ell R = 0.04$, $P_o H_{DLC} = 0.453$).

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detailed analysis of the resulting stress data on the individual nodes reveals that the maximum values of the equivalent stress at various depths lie on a line with the coordinate of $x \approx 0.0125a$, which has negligible deviation from the central line of the contact region. Also, a comparison between the maximum values along these two positions (i.e., $x \approx 0.0125a$ and $x = 0$) shows no significant change. Thus, the analysis of spatial equivalent stress distribution can be reasonably simplified by only considering the equivalent stress distribution along the $z$ axis.

The analysis of yielding is based on comparing the calculated equivalent stress distribution and the yield strength profile in the near surface region of the substrate given in Figure 33. The location of the initial yielding point, $z_0$, coincides with the location of the maximum calculated equivalent stress. Also, the depth of the yielding region along the $z$ axis, $\Delta z_0$, depends on the portion of which the calculated equivalent stress is higher than the local yield strength of the graded layer. This approach is schematically illustrated in Figure 35 with the profiles of the calculated equivalent stress and yield strength of the graded substrate for the case of indentation with no coating present ($L/R = 0, P_0 H_{DLN} = 0.38$).

It is interesting to note that the interface with gradient in strength dramatically decreases the size of the yielding zone, $\Delta z_0$, compared with the original (unprocessed) substrate under the same loading condition. Also, proper design of the substrate graded layer can completely prevent plastic deformation in the substrate (profile 2 in Figure 35).

**Initiation of yielding** The normalized location of the initial yielding point under friction, at various levels of coating thickness and contact stress is shown in Figure 36 (a). It is shown that the maximum contact stress ($P_0$) does not exercise any influence on

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Figure 35 Profiles of calculated equivalent stress and yield strength of graded and ungraded substrates.
Figure 36  (a) Location of initial yielding as a function of contact stress and (b) Relation between location of initial yielding and coating thickness.
the value of $\alpha$, while the coating thickness has a significant effect. It is also shown that for an uncoated substrate ($t/R = 0, f = 0.1$), yielding occurs below the surface at a depth range of $0.65\alpha$ which is very close to the yielding location predicted by the von Mises yield criterion for indented non-layered media without friction ($0.67\alpha$) [140]. The small difference is more than likely brought by the applied tangential friction force, which is consistent with the previous calculations [173]. For thin coatings, $t/R = 0.02, 0.04$, yielding initiates in the substrate beneath the contacting region and at a depth of $0.40\alpha$ and $0.22\alpha$, respectively. For thicker coatings, $t/R = 0.07, 0.1$, yielding starts on the coating/substrate interface, regardless of the of $P_0H_{DLC}$ value. In fact, careful analysis reveals that in the case of thick coatings, the peak values of von Mises equivalent stress (as shown in Figure 35) locate inside the coating. However, for a brittle coating such as DLC, plastic flow prior to fracture in the coating should be neglected, thus it is considered that yielding starts on the coating-substrate interface. On the other hand, in the case of a hard and tough coating, plastic deformation prior to fracture becomes feasible. In the latter case, plastic flow should start in the coating provided the its yield strength is exceeded by the maximum von Mises equivalent stress.

A more clear expression of the relationship between normalized initial yielding location and the normalized coating thickness is given in Figure 36 (b). It is evident that for a thin coating ($t/R \leq 0.07$), yielding starts in the substrate while for a thick coating ($t/R \geq 0.07$), yielding starts on the coating/substrate interface (corresponding to $z_0/\alpha = 0$) for brittle coatings, or in the coating if it can deform plastically. Usually, for a brittle coating (such as DLC), plastic flow near or at the interface may initiate nucleation and growth of cracks along the interface due to its inability to follow the deflection of the
substrate. The interfacial delamination of the coating will be generated by this plastic flow and followed by crack growth along the interface. Also, the intrinsic highly compressive stress present in such coatings (> 4 GPa) and their brittle nature can trigger the initiation and growth of cracks within the coating [146]. Thus, as the coating thickness increases, the stored elastic strain energy builds up to a critical level that can cause either coating delamination from the substrate or cracking of the coating itself. As a result, deposition of thick hard coatings is not recommended in such cases.

Growth of the yielding zone in the substrate The normalized size of the yielding zone, \( \Delta z_0/a \), under various values of \( t/R \) and \( P_o/H_{DLC} \) is illustrated in Figure 37 (a). The size of the zone grows by increasing the external contact stress or decreasing coating thickness. In addition, it is evident that the growth rate of the yielding zone, which can be expressed by the differential \( d(\Delta z_0/a)/d(P_o/H_{DLC}) \), increases considerably with contact stress \( P_o/H_{DLC} \). This indicates that significant plastic flow will occur in the substrate at large values of external contact stress. Consequently, hard and brittle coatings such as DLC could be fractured by the plastic deflection of the substrate.

The intercepts of the curves in Figure 37 (a) with the \( P_o/H_{DLC} \) axis indicate the values of \( P_o/H_{DLC} \) for \( \Delta z_0/a = 0 \), which can be considered the critical contact stress, \( P_{cr}/H_{DLC} \), for the occurrence of yielding under different values of coating thickness. The correlation of normalized critical applied stress, \( P_{cr}/H_{DLC} \), with normalized coating thickness, \( t/R \), is shown in Figure 37 (b). It can be seen that the minimum value of \( P_o/H_{DLC} \) for the onset of yielding increases with the coating thickness, and an approximately linear relation is found. This is probably due to the higher load carrying...
Figure 37  (a) Variation of yield zone size with $P_o H_{DLC}$ for various values of coating thickness (b) Relation between critical contact stress for yielding and $t/R$. 

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capacity of the hard coating than that of a soft substrate. In brief, the resistance to yielding of a coated substrate can be improved by proper selection of coating thickness.

Figure 38 shows the variation of maximum calculated equivalent stress in the substrate as a function of $P_0/H_{DLC}$ and $t/R$. It can be seen that for any coating thickness, the ratio of maximum equivalent stress in the substrate to contact stress, $\sigma_{max}/P_0$, shows a small variation and falls within the range of 0.57 to 0.65. This calculation result suggests that the maximum equivalent stress in the substrate increases proportionally with the contact stress regardless of coating thickness.

The combination of Figures 36, 37 and 38 provides the required depth and yield strength profile of the graded zone to prevent local yielding in the substrate under various values of coating thickness and contact stress.

As discussed above, under the combination of normal and tangential traction, yielding initiates at a certain depth in the substrate, depending on the coating thickness. As the contact stress increases, the local yielding zone grows in two directions, into the substrate and towards the coating/substrate interface. At a critical value of contact stress ($P_{crit}$), the yielding zone will reach the interface. This interaction of the plastic zone with the interface may be crucial, since it can create sufficient interfacial deflection to trigger fracture of the brittle coating. Figure 39 shows the correlation between the critical normalized contact stress, $P_{crit}/H_{DLC}$, for the interaction of the plastic zone with the interface, and the normalized coating thickness. It is evident that a higher critical stress is required for thin coatings since as the coating thickness decreases, the initial yielding point is moving further away from the interface, Figure 36 (b). However, after a certain coating thickness $P_{crit}/H_{DLC}$ increases due to high load carrying capacity of the

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Relation between maximum von Mises stress and contact stress.
Figure 39 Relation between critical contact stress required for plastic zone to reach the interface and coating thickness.
hard coating and hence high contact stress required for initiating yielding. Figure 39 presents this variation along with the value of \( t/R \approx 0.07 \) corresponding to minimum \( P_{cri}/H_{DLC} \).

The influence of coating thickness and maximum contact stress on the growth of the yielding zone in both \( x \)- and \( z \)-directions is shown in Figure 40. Figure 40 (a) displays the boundaries between elastic and plastic regions in the substrate as a function of coating thickness \( (t/R = 0.02 \text{ and } 0.04) \) under the same contact stress \( (P_0/H_{DLC} = 0.453) \). It can be seen that under the same contact stress, a thick coating results in a shallow but wide (on the interface) plastic zone. On the other hand, a thin coating results in a deep but narrow plastic zone. The results indicate that thick coatings can limit plastic zone development in depth while thin coatings in width (on the interface).

Figure 40 (b) shows the boundaries between the elastic and plastic regions in the substrate for two values of contact stress \( (P_0/H_{DLC} = 0.286 \text{ and } 0.453) \) for the same coating thickness \( (t/R = 0.07) \). It is evident that contact stress exhibits a profound influence on the growth of plastic zone in both \( x \)- and \( z \)-directions. The relation shown in Figures 40 (a) and (b) can be used to determine the approximate location and size of the plastic zone for a given combination of coating thickness and contact stress or alternatively to select the coating thickness to minimize yielding effects.

**Effect of friction coefficient on yielding behavior**

Equivalent stress calculations were also conducted for different values of friction coefficient \( (f = 0, 0.25 \text{ and } 0.50) \). Due to the distortion of the equivalent stress contour under a higher friction coefficient, the maximum equivalent stress profile does not coincide with the central line \((z \text{- axis})\). The profiles of the von Mises equivalent stress were plotted along the \( x \)-direction for various depths within the substrate. The maximum value and its
Figure 40  
(a) The effect of coating thickness on the growth of plastic zone ($P_o H_{DLC} = 0.453$)  
(b) The effect of contact stress on the growth of plastic zone ($t R = 0.07$).
corresponding deviation from the z-axis were obtained and plotted with respect to depth. The initial yield location and the size of the yielding zone were determined by comparing the maximum equivalent stress profile and the yield strength profile of the graded layer.

The influence of the friction coefficient on the initial yielding location is schematically shown in Figure 41 (a). It can be seen that as \( f \) increases, the initial yielding location moves in the \(+x\)-direction toward the interface. This can be attributed to the increasing tangential traction under the same normal contact stress. A similar conclusion has been reached in previous studies [138,173]. Due to the same reason, the yielding zone along the \( z \)-direction expands with increasing \( f \), as shown in Figure 41 (b).

**Influence of coating/substrate elastic modulus ratio** The coating/substrate modulus ratio was also varied to study its effect on the yielding behavior of the substrate. In fact, large variations in Young's modulus of DLC coatings (from <100 GPa up to >500 GPa) have been observed due to different fraction of \( sp^3 \) and \( sp^2 \) bonding in the DLC structure [174].

Figures 42 (a) and (b) present the effect of elastic modulus ratio, \( E_c/E_s \), (\( E_c \) and \( E_s \) are the elastic modulus of the coating and substrate, respectively) on the normalized initial yielding point and the normalized width of plastic zone, respectively. It can be seen that high ratios of elastic modulus shift the initial yielding point closer to the coating/substrate interface. A relatively high elastic modulus of the coating increases the deflection difference between the coating and substrate and as a result creates a high stress concentration in the region near the coating/substrate interface. Thus, in the case of a high modulus ratio, yielding of the substrate initiates in the region near the coating/substrate interface.
Figure 41 The effect of friction on (a) the location of initial yielding, and (b) the size of plastic zone ($P_0 H_{DLC} = 0.453$).
Figure 42  The effect of the coating/substrate modulus ratio on (a) the initial yielding location, and (b) the size of yield zone ($\nu/R = 0.02$, $P = 50$ kN/m)
From the plot in Figure 42 (b), it can be seen that for the same coating thickness, a higher modulus ratio develops a larger yielding zone within the substrate. This can be considered in two incidents of coating/substrate combinations: (i) a reduction in the elastic modulus of the substrate while the modulus of the coating remains constant; and (ii) increasing in the modulus of the coating while that of the substrate remains constant. In the former case, the yielding zone expands due to lower load carrying capacity of the substrate and in the latter case, the contact region between the indenter and coating decreases thus increasing the contact stress and consequently, the depth of the yielding zone within the substrate, Figure 37 (a).

Effect of gradient in elastic modulus on the stress distribution Multilayers possess high potential in advanced tribological systems since they can improve the adherence between a hard coating and its substrate [49]. An innovative concept is to develop a gradient in the elastic modulus that can be produced by depositing thin layers of different composition or different thickness creating a graded composite layer. In this study, a gradient composite is assumed to be constructed of 8 layers (the thickness of each layer = \(a\)) deposited on a soft substrate (e.g., Ti-6Al-4V alloy) and exhibiting a linear variation in the elastic modulus. A hard coating (\(E_c/E_s = 4, \nu/R = 0.02\)) is deposited on top of the gradient layer. The variation of the elastic modulus for this multilayer system is described in Table 11.

Figure 43 presents the equivalent stress distribution along the center line of the contact region for a system with and without a gradient in the elastic modulus (\(P_o/H_{DLC} = 0.527, f = 0.1, t/R = 0.02\)). For the ungraded substrate, there are two peak values for the equivalent stress, which are located on the contact surface and in the substrate at a depth
Table 11  Elastic modulus variation in the graded layer

<table>
<thead>
<tr>
<th>Depth</th>
<th>0~a</th>
<th>a~2a</th>
<th>2a~3a</th>
<th>3a~4a</th>
<th>4a~5a</th>
<th>5a~6a</th>
<th>6a~7a</th>
<th>7a~8a</th>
</tr>
</thead>
<tbody>
<tr>
<td>E (GPa)</td>
<td>433.5</td>
<td>390.9</td>
<td>348.2</td>
<td>305.6</td>
<td>262.9</td>
<td>220.3</td>
<td>177.7</td>
<td>135.0</td>
</tr>
</tbody>
</table>

Figure 43  The distribution of equivalent stress in the presence of graded and ungraded substrate layer ($t R = 0.02, P_o H_{BLE} = 0.572, f = 0.1$).
of 0.367a. It can be seen that the equivalent stress on the contact surface is dramatically increased due to high stress concentration. Thus, under this condition, degradation more than likely will occur on the coating surface by crack initiation, propagation through the thickness of the coating and consequently delamination from the substrate. Meanwhile, yielding occurs within the substrate, which may accelerate the deflection and failure of the hard coating.

In the case of the graded substrate, the calculated equivalent stress on the contact surface is significantly decreased due to the uniform distribution of the elastic modulus across the coating/substrate region. Also, a slight reduction in the maximum value of equivalent stress within the substrate is observed. Thus, if a modulus gradient is developed in the substrate, yielding can be restricted or even avoided at the location of maximum equivalent stress. In brief, a more uniform stress distribution develops in the coating/substrate region in the presence of gradient in elastic modulus.

D. Tribological Behavior of Duplex Nitriding/DLC Coating Treatments

1. Growth kinetics of nitrided layer

The microhardness profiles of Ti-6Al-4V specimens processed by intensified plasma nitriding (IPAP) for 4 and 9 hours are shown in Figure 44 (a). These specimens were processed at 50 mTorr N₂ pressure, 2 kV bias voltage and 1 mA/cm² current density. These conditions were selected since they produce a nitrided surface with relatively low roughness. The nitriding depths of the specimens processed for 4 and 9 hours were found to be 35 µm and 55 µm, respectively. The growth kinetics of the
nitriding depth for the aforementioned processing conditions is presented in Figure 44 (b). As expected a linear relationship exists between the growth of the nitrogen diffusion layer and the square root of time showing a volume diffusion-controlled process. Similar observations have been made previously for intensified and conventional plasma nitriding [175] with the difference that the intensified process exhibits much faster kinetics [153].

2. The size of the plastic zone in DLC-coated Ti-6Al-4V alloy under indentation

As stated earlier, pin-on-disc friction tests were conducted to investigate the tribological behavior of duplex DLC coating/nitriding treatments. In the friction tests, \( \text{Al}_2\text{O}_3 \) was selected as the pin material with a diameter of 9.5 mm \((E = 343 \text{ GPa}, \, \nu = 0.25)\), and three loading levels (1 N, 2.5 N and 5 N) were applied. The selected thickness for the DLC coating was \( \sim 0.4 \mu\text{m} \), and under this condition, the initial yielding point should be in the substrate, Figure 36. The contact between a ball and a flat surface is in the axisymmetric condition which is somewhat different from the condition of plane strain, therefore, the previous analysis related to the size of plastic zone during indentation of a cylindrical pin on a flat surface needs to be modified. A theoretical analysis was performed on the complete stress field due to a circular contact region carrying a "hemisphere" Hertzian normal pressure and proportionally distributed shearing traction [135]. It was assumed that during indentation of a sphere on a flat surface, the stress distribution on the contact surface is in a the elliptical form:

\[
P(r) = P_0 \sqrt{1 - \frac{r^2}{a^2}} \quad \text{(for } r \leq a),
\]

(17)
Figure 44. (a) Microhardness profiles of nitrided Ti-6Al-4V, (b) The growth kinetics of nitrogen diffusion zone.

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where $P_0 = \frac{3P}{2\pi a^2}$, $P$ is the external load) is the maximum contact stress at the center of the contact region, and $a$ is the contact radius. Assuming contact of the $\text{Al}_2\text{O}_3$ ball with the flat DLC-coated surface and neglecting the influence of the substrate properties, the values of $P_0$ and $a$ under 1 N, 2.5 N and 5 N can be calculated using the methods given in Appendix I, and listed in Table 12.

Under the boundary condition given by equation 17 and ignoring the effect of tangential traction due to low friction of DLC coating, the normalized tensile stress along the center line of contact region (z-axis) can be expressed by [135]

\[
\frac{\sigma_{xz}}{P_0} = \frac{\sigma_{zy}}{P_0} = (1 + \nu)[1 - \frac{z}{a}\tan^{-1}\left(\frac{a}{z}\right)] + \frac{1}{2}(1 + \frac{z^2}{a^2})^{-1} \tag{18a}
\]

\[
\frac{\sigma_{zz}}{P_0} = (1 + \frac{z^2}{a^2})^{-1} \tag{18b}
\]

The distribution of normalized von Mises equivalent stress derived from equations 18(a) and 18(b) is shown in Figure 45 (a) and the real values of von Mises equivalent stress in DLC-coated Ti-6Al-4V alloy are plotted in Figure 45 (b) for external loading levels 1 N, 2.5 N and 5 N. The intercepts of the plots with the stress value 1.04 GPa (yield strength of Ti-6Al-4V alloy), $\Delta z/a$, are 6.2, 7.6 and 9.6 corresponding to loading level 1 N, 2.5 N and 5 N, respectively, which gives the approximate size of the plastic zone under those loading levels, $\Delta z = 4.57 \mu m, 7.60 \mu m$ and $12.1 \mu m$, respectively.

It should be noted that the above analysis is based on the assumption of uniform material (without coating) which is reasonable in view of the small thickness of the
Table 12  The values of contact radius, max. contact stress between Al₂O₃ and DLC/nitried Ti-6Al-4V alloy

<table>
<thead>
<tr>
<th>External loading (N)</th>
<th>Contact radius (μm)</th>
<th>Max. contact stress (P₀, GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.74</td>
<td>879</td>
</tr>
<tr>
<td>2.5</td>
<td>1.00</td>
<td>1194</td>
</tr>
<tr>
<td>5</td>
<td>1.26</td>
<td>1504</td>
</tr>
</tbody>
</table>

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Figure 45. (a) Normalized $\sigma_{vm}$ distribution along the centerline, (b) $\sigma_{vm}$ distribution along the centerline.
coating. According to the FE modeling, in the case of indentation in a hard coating/soft substrate system, due to the higher load carrying capacity of the hard coating, the size of plastic zone within the substrate can be decreased compared with the case without coating, Figure 37. Thus, the estimated sizes of plastic zone for the indentation of spherical Al₂O₃/DLC coated Ti-6Al-4V alloy are the upper limits of the plastic zone in the substrate under various loading levels.

3. Determination of the nitriding depth

The plastic deformation of the surface region in the substrate during loading should be prevented in order to accommodate the hard DLC coating. Based on the size of plastic zone under the present loading levels estimated in the previous section, the depth of nitrogen diffusion zone need to be ≥ 12 μm. The optimum operational parameters for the nitrogen diffusion process by IPAP have been obtained from the results of the preliminary experimental study. Two nitriding depths of ~15 and ~30 μm were developed in the present study to investigate the effect of the depth of the hardened zone on the tribological behavior of DLC films. According to the kinetic study (Figure 44 (b)), these two values of nitriding depth are approximately corresponding to the nitriding time of about 1 hour and 4 hours, respectively.

All friction testing on DLC/nitrided Ti-6Al-4V alloy was conducted at a sliding velocity of 0.3 m/s, at room temperature (~25° C) and under room humidity (~40%) in order to minimize the influence of these parameters on the graphitization process of DLC coatings. The total sliding distance for all tests was 10 km or until the DLC coatings

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failed. Also, the characterization of wear track was conducted using the same methods described before.

4. Friction behavior of duplex nitriding/DLC coating treatments

The measured Knoop hardness of as-deposited DLC coating was 2366 (10 g load) which is corresponding to 28 GPa and is very close to the hardness value of DLC films produced by IBD [156]. Friction tests were conducted for three different duplex treatments: (i) DLC coating/Ti-6Al-4V alloy (unprocessed); (ii) DLC coating/Ti-6Al-4V alloy with 15 μm nitrided zone; (iii) DLC coating/Ti-6Al-4V alloy with 30 μm nitrided zone. The results from the friction tests are summarized in Table 13. In this study, the durability of the DLC film is defined as the sliding distance, $S_f$, required for the DLC film to fail.

Several interesting observations can be made by analyzing the results shown in Table 13. For example, for samples with the same treatment it was found that the wear rate of the pin increases by increasing loading level. This can be attributed to the larger contact area between pin and disc due to higher external loading. Also, the wear rate of the pin depends on the hardness of the counter-face, i.e., DLC/substrate system. The comparison of the wear rate of the Al$_2$O$_3$ pin among Tests 2, 5 and 8 (0.173x10$^{-8}$mm$^3$m$^{-1}$N$^{-1}$, 0.366x10$^{-8}$mm$^3$m$^{-1}$N$^{-1}$ and 0.375x10$^{-8}$mm$^3$m$^{-1}$N$^{-1}$, respectively), and among Tests 3, 6 and 9 (0.187x10$^{-8}$mm$^3$m$^{-1}$N$^{-1}$, 0.843x10$^{-8}$mm$^3$m$^{-1}$N$^{-1}$ and 1.07 x10$^{-8}$mm$^3$m$^{-1}$N$^{-1}$, respectively) indicates that the substrate hardening increases the overall hardness of the counter-face that has as a result the progressive increase of the pin wear rate. Considering a thin DLC coating deposited on nitriding hardened surface, the strength
Table 13  Friction tests of Al₂O₃/DLC-coated Ti-6Al-4V and nitrided Ti₄Al-4V alloy.

<table>
<thead>
<tr>
<th>Test sample (Al₂O₃ pin)</th>
<th>Test No</th>
<th>Load (N)</th>
<th>σᵧ (MPa)</th>
<th>f_m</th>
<th>f_w</th>
<th>S_f (km)</th>
<th>Huable (%μm)</th>
<th>H_f (%μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>i. DLC/ Ti-6Al-4V</td>
<td>1</td>
<td>1</td>
<td>513</td>
<td>0.14</td>
<td>0.20</td>
<td>&gt;10</td>
<td>UD</td>
<td>2.28</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.5</td>
<td>697</td>
<td>0.17</td>
<td>0.15</td>
<td>6.12</td>
<td>0.173</td>
<td>3.54</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>5</td>
<td>878</td>
<td>0.14</td>
<td>0.11</td>
<td>3.67</td>
<td>0.187</td>
<td>2.75</td>
</tr>
<tr>
<td>ii. DLC/ nitrided Ti-6Al-4V (15 μm)</td>
<td>4</td>
<td>1</td>
<td>513</td>
<td>0.04</td>
<td>0.08</td>
<td>&gt;10</td>
<td>UD</td>
<td>2.75</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>2.5</td>
<td>697</td>
<td>0.13</td>
<td>0.17</td>
<td>6.44</td>
<td>0.366</td>
<td>3.37</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>5</td>
<td>878</td>
<td>0.10</td>
<td>0.12</td>
<td>5.96</td>
<td>0.843</td>
<td>3.09</td>
</tr>
<tr>
<td>iii. DLC/ nitrided Ti-6Al-4V (30 μm)</td>
<td>7</td>
<td>1</td>
<td>513</td>
<td>0.10</td>
<td>0.15</td>
<td>&gt;10</td>
<td>UD</td>
<td>2.29</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2.5</td>
<td>697</td>
<td>0.13</td>
<td>0.18</td>
<td>8.91</td>
<td>0.375</td>
<td>3.13</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>5</td>
<td>878</td>
<td>0.12</td>
<td>0.15</td>
<td>6.58</td>
<td>1.07</td>
<td>2.34</td>
</tr>
</tbody>
</table>

S_f: sliding distance before failure of DLC coating. UD: undetectable.
The definitions of other parameters are same with those in Table 9.
response of the layered system to the indentation by a high load is influenced by the properties of the substrate [176]. The degree of the influence depends on the ratio of the coating thickness and indentation depth. For the same coating thickness, higher loading level results in a larger indentation depth and thus increases the effect of substrate properties on the friction behavior. This effect can be seen by comparing pin wear rates at the same loading for the various treatments (increasing substrate hardness).

As revealed by the data in Table 13, for samples within the same treatment, increasing loading level decreased the lifetime ($S_f$) of the DLC coating. It has been found that the primary cause of failure of DLC films during friction is delamination from the substrate [108]. According to the previous FE analysis, when external loading is applied to a thin film/graded substrate system, yielding initiates at a certain depth in the substrate, and gradually grows in both directions i.e., into the substrate and towards the coating/substrate interface. When the yielding zone reaches the interface, it will create interfacial deflection of the substrate. Because of the mismatch of the deflection between the hard DLC film and soft substrate during indentation and friction, microcracks can nucleate at the DLC/substrate interface causing film delamination. Furthermore, based on the profiles of the elastic/plastic boundaries shown in Figure 40 (b), it can be seen that a higher external contact stress increases the plastic region at the interface. Thus, under higher external loading, microcrack nucleation at the interface is easier reducing film durability.

Another interesting observation was that the wear rate of the DLC film in all tests did not exhibit any significant variation (wear rates were determined based on film durability, $S_f$, and varied between $2 - 3 \times 10^{-7} \text{mm}^3\text{m}^{-1}\text{N}^{-1}$). This observation suggests that
surface treatment of the substrate does not exercise a significant influence on the wear rate of the DLC coating. Since the sputtered Si interlayer can form strong chemical bonding with DLC structure and thus enhance the adhesion between DLC film and its substrate, the wear rate of DLC coating only depends on its as-deposited structure and residual stress, as proposed in a previous study [114]. However, the surface treatment has a major effect on the failure mechanism as is discussed later in this section.

Tests 1, 4 and 7 show the tribological behavior of DLC/nitrided substrate system under low loading level (1 N). The results showed that for the present total sliding distance (10 km) the durability of the DLC films is not affected by the substrate surface treatment. Additionally, the wear of the Al₂O₃ pin was negligible. Based on the information provided in Figures 37 (a) and 39, it is evident that under a low external contact stress the substrate plastic deformation is limited (if any). These conditions allow the interface region to operate mainly in the elastic regime and no effect from substrate hardening can be realized. Thus, in this case lifetime of the film is a result of the gradual wearing out of the coating by the hard Al₂O₃ pin.

Under medium loading (2.5 N), DLC film durability was found to increase with substrate hardening (6.12 km, 6.44 km and 8.91 km, for unprocessed, 15 μm and 30 μm nitrided zone, respectively). The observed increase in durability indicates that the modified substrate has a positive impact on the tribological behavior of the DLC coatings. Based on the FE analysis, substrate hardening has two major effects. It can effectively reduce (or even eliminate) the plastic zone size and restrict its growth by not allowing it to reach the coating/substrate interface, Figure 35. This is evident by the
observed 5.2% and 45.6% higher durability produced by the 15 μm and 30 μm nitrided zone, respectively.

Tests 3, 6 and 9 exhibit the tribological behavior of DLC/nitrided substrate system under high loading level (5 N). Compared with the durability of DLC/untreated substrate (3.67 km), development of a nitrided zone produced significant improvements (5.96 km and 6.58 km, for 15 μm and 30 μm nitrided depth, corresponding to 62.4 % and 79.3 % improvement, respectively). It is evident from these results that increasing the loading level makes the effect of the substrate hardening more pronounced.

In brief, the lifetime of DLC with the FGI produced by nitriding process are significantly improved, compared with that of DLC/unprocessed substrate. More enhancement on the durability of DLC coating is found under high loading level. This experimental response is consistent with the FE analysis in this research.
VI. SUMMARY

The present research has concentrated on three aspects related to the tribological behavior of DLC coatings. Based on the results, the following conclusions can be derived:

A. Tribological Behavior of DLC Film

- The as-deposited DLC films produced by IBD have high hardness (30 GPa), low friction coefficient ($f_{\text{init}}$: 0.12-0.20, $f_{\text{fin}}$: 0.06-0.08) and low wear rate ($1.6\times10^{-9}$ mm$^3$/mN).
- The characterization showed that as-deposited DLC is dense and featureless. ED pattern analysis revealed a mainly amorphous structure with evidence of short range $sp^3$ diamond cubic domains with a lattice parameter of about 3.64 Å.
- Pin-on-disc friction tests conducted on DLC films showed three distinct regimes: initially a break-in period, an intermediate constant friction plateau of a relatively short duration and a steady-state stage with further reduced values of $f$ ($f < 0.08$).
- The experimental evidence suggests that the intermediate friction plateau is mainly due to transfer layer formation (occurring by the destabilization of DLC during the break-in stage), whereas the occurrence of steady-state is related to the formation of a graphitized tribolayer.
- Analysis of the transfer layer and wear debris showed that they contain graphite particle clusters. The morphological analysis of the formed graphite indicates that the graphitization of DLC occurred at "hot spots" during asperity contact.
• The transformation is suggested to proceed with a precursor hydrogen atom release stage and shear deformation that converts the $(111)_{\text{DLC}}$ into $(00.2)_{\text{GR}}$ planes facilitating the nucleation of graphite. The low $f$ and wear rate observed during testing of DLC is attributed to the low shear strength of the hexagonal graphite planes. A wear-induced graphitization mechanism was proposed based on the above processes.

• Operational parameters (sliding velocity and loading level) and environmental parameters (humidity and temperature) influence the graphitization process and thus the DLC tribological behavior. The results showed that sliding velocity exercises a stronger influence than loading level. This is attributed to the greater effect of contact frequency on the temperature rise at asperities facilitating hydrogen release from the DLC structure which is the prerequisite for the wear-induced graphitization process. A predictive equation was developed to describe the formation rate of the graphitized tribolayer during the wear process taking into consideration the aforementioned wear parameters. Increasing the level of environmental humidity was found to decelerate the graphitization process. This can be attributed to the condensed water layer on the contact interface that may prevent generation of high flash temperatures, prevent release of hydrogen atoms, and affect the integrity of the tribolayer. At low environment temperature no graphitization was observed since higher thermal conduction and convection rate can cool down the "hot spots" rapidly and suppress nucleation of graphite on "hot spots". However, elevated temperatures can accelerate the graphitization rate more than likely by promoting hydrogen release from the DLC structure.
B. FE Modeling for Yielding Behavior of Hard Coating/Graded Substrate System

- The graded interface produced by surface hardening using plasma nitriding can dramatically decrease the size of the yield zone compared with the original substrate.

- The initial yielding location, \( z_0a \), depends on the coating thickness, but not on the contact stress. As coating thickness increases the location approaches the coating/substrate interface.

- The size, \( \Delta z_0a \), and growth rate, \( \frac{d(\Delta z_0a)}{d(P_o/H_{DLC})} \), of the yielding zone increase with increasing contact stress, and the critical contact stress for the onset of yielding increases with coating thickness.

- As the friction coefficient increases, the initial yield location, \( z_0a \), moves toward the coating/substrate interface along the sliding direction, meanwhile, the normalized size of plastic zone, \( \Delta z_0a \), increases.

- A higher coating/substrate modulus ratio brings the initial yield location toward the coating/substrate interface and increases the size of the plastic zone.

- Development of a multilayer system producing a gradient in the modulus was found to result in a reduction of the maximum equivalent stress on the contact surface and in the substrate. Both of these effects are expected to have a beneficial impact on the tribological behavior of the hard coating.
C. Tribological Behavior of Duplex Nitrogen Diffusion/DLC Coating Treatments

- Substrate hardening by intensified plasma nitriding developed a FGI that was found to positively impact on the durability of DLC coatings.
- At low external loading, the FGI had a small effect on durability of DLC because the interfacial region of the coating/substrate system is mainly in the elastic regime. In this case the lifetime of the DLC coating is determined by the wear process that is gradually consuming the film.
- At higher loading levels, the presence of the FGI resulted in a progressively more significant effect that reaches an improvement of about 80% in durability for the loading levels applied in the present study. These positive effects are attributed to the reduction of the plastic zone size developed in the substrate and the prevention of yielding from reaching the coating/substrate interface. Thus, substrate hardening by intensified plasma nitriding provides the means for the development of an effective FGI that can affect the yielding behavior of the substrate.
REFERENCES


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[71]. J. Kumar, J. Han, E.A. Starke, Jr and K. O. Legg, Scripta Metall., 17 (1983) 479.


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During contact between a ball and a flat surface, the radius $a$ (in meter) of the equivalent circular contact area for the case of a sphere on a flat plate is given by [178]

$$a = 0.0182 \sqrt[3]{PK_D C_E},$$

where $P$ is the external applied load (in Newton), $K_D$ is the equivalent diameter (in meter) and for the present case $K_D = D$ where $D$ is the diameter of the pin and $C_E$ (Pa\(^{-1}\)) is calculated by

$$C_E = \frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2},$$

where $E_1$ and $E_2$ are the elastic modulii of the two materials in contact and $v_1$ and $v_2$ are the values of the Possion's ratio of the pin and substrate material, respectively.

Under contact, the Hertzian stress $\sigma_H$ between the ball material and the flat surface (sphere on flat plate geometry) can be calculated by

$$\sigma_H = 0.41 \sqrt[3]{\frac{PE_{\text{eff}}^2}{d^3}},$$

where $d$ is the diameter of the pin and $E_{\text{eff}}$ is given by

$$E_{\text{eff}} = \frac{2}{\frac{1 - v_1^2}{E_1} + \frac{1 - v_2^2}{E_2}}$$

the parameters in the above equation have been previously defined.
APPENDIX 2

Considering the case of contact between two cylinders whose longitudinal axes are parallel and that in contact along a line, the value of $a$, the half width of contact area, can be found from the equation [179]:

$$a = \sqrt{\frac{2P\Delta}{\pi}},$$

in which $P$ is the normal load per unit length, and

$$\Delta = \frac{1}{\frac{1}{2} \left( \frac{1}{R_1} + \frac{1}{R_2} \right)} \left[ \frac{1 - \nu_1^2}{E_1} + \frac{1 - \nu_2^2}{E_2} \right].$$

The symbols $R_i$, $\nu_i$ and $E_i$ represent the radius, Poisson's ratio and elastic modulus, respectively for one cylinder. $R_2$, $\nu_2$ and $E_2$ have similar meaning for the second cylinder.

The maximum contact stress on the center of contact area, $p_0$ can be obtained by:

$$p_0 = \frac{2P}{\pi a}.$$
APPENDIX 3
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Yan Liu was born on March 15, 1967 in Beijing, China. She received her Bachelor of Science in Mechanical Engineering from Xi’an Jiaotong University, China, in July, 1985. She attended graduate school at Xi’an Jiaotong University in September, 1985, and obtained a Master of Science degree in Materials Science and Engineering in June, 1988. She worked as a research engineer in Theory of Lubrication and Bearing Institute, China, from July 1988 to October, 1993. She began graduate work in the Materials Science and Engineering Program, Mechanical Engineering Department, Louisiana State University, in January, 1994. She is currently a candidate for the degree of Doctor of Philosophy in Engineering Science to be awarded at the Fall commencement, 1997.
DOCTORAL EXAMINATION AND DISSERTATION REPORT

Candidate: Yan Liu

Major Field: Engineering Science

Title of Dissertation: Tribological Behavior of Duplex Nitrogen Diffusion/DLC Coating Treatments

Approved:

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:
August 22, 1997