

IBM Research Report

Friction in Amorphous Diamondlike Carbon

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A. INTRODUCTION

Since Enke et al. [1] first reported in 1980 that diamondlike carbon (DLC) films deposited from acetylene have very low friction coefficients, DLC films are considered in general as materials with very low friction coefficients and as potential solid lubricants. However, this generalization is oversimplified. A compilation of friction coefficients (μ) of DLC films [2] shows that they span a large range of values, from $\mu=0.002-0.4$ in vacuum below 10^{-4} Pa, to $\mu=0.05-1.00$ in ambient air, at relative humidities of $20\% < RH < 60\%$. Most typical, however, are the ranges $\mu=0.007-0.02$ in vacuum and $\mu=0.1-0.4$ in ambient air. The large spread in the values of the friction coefficients can be understood if one takes into account the fact that the DLC term describes a large group of materials whose composition, structure and properties are affected by the deposition system, i.e. the used precursors, deposition method, and deposition conditions. The measured friction coefficients are, therefore, strongly dependent on the system used for the deposition of the specific films and are affected by the testing conditions. This dependence is illustrated in the diagram shown in FIGURE 1. The *deposition system* determines the properties of the bulk of the film and of its surface. The *tribological system*, which includes the counterpart used in the friction and wear measurement, the Hertzian pressure, the relative speed between the sliding parts and the ambient, determines the testing conditions, which in turn affect the measured friction values.

(*Insert FIGURE 1*)

Detailed reviews of the tribology of DLC and its modifications can be found elsewhere [3,4], therefore the following will present only an updated summary of the frictional properties of DLC materials. The friction between surfaces in contact is affected by a variety of factors, however, it is controlled mainly by the formation and breaking of chemical bonds at the interface between the moving parts [5]. Crystalline diamond is characterized by a low friction coefficient which depends strongly on the environment and is mainly controlled by surface dangling bonds. Diamond has a low friction coefficient in humid air or dry nitrogen, due to a contaminant layer of low shear strength. In contrast, clean diamond surfaces can interact strongly producing high friction coefficients. Thus, the friction coefficient of diamond against diamond in vacuum can increase to values as high as 1.0 when the surface hydrogen is desorbed, leaving interacting dangling bonds [5]. Saturation of the dangling bonds by atomic hydrogen or other adsorbates reduces the friction coefficient of diamond to $\mu=0.02$. Water [6,7] and atomic hydrogen [8] act as lubricants also for graphite and improve its wear and lubricating behavior.

DLC films deposited by plasma enhanced chemical vapor deposition (PECVD) have several common tribological characteristics [3,4]: (i) they display a behavior similar to diamond in

ultrahigh vacuum (UHV) but not in humid atmosphere; (ii) the friction coefficient of hydrogenated DLC is low in humid nitrogen or oxygen, extremely low in dry nitrogen or UHV, and, sometimes, very high in dry oxygen; (iii) loss of hydrogen through annealing at high temperature causes a marked increase in the friction coefficient of DLC in UHV, but not in humid environment; (iv) both friction and wear of DLC are usually affected by a transfer layer which forms in most cases during friction.

B. TRIBOCHEMICAL EFFECTS

It has become clear that the wear and friction of DLC films are controlled by complex tribochemical mechanisms that are in turn affected by the surface chemistry of the films. The latter is dependent on the method used for the preparation of the films and on the testing conditions (FIGURE 1). The transfer layer mentioned above is usually formed by a friction induced transformation of the top layer of the DLC film into a material of low shear strength. This transformation may be caused by thermal and strain effects generated during sliding [9]. The composition of the transfer layer and its shear strength is determined by the nature of the investigated DLC film, the material of the sliding counterpart, the testing ambience, contact load, and sliding speed. The low friction and ultralow wear of DLC and counterparts can be attributed to the low shear strength of this transfer layer [10]. The existence of a transfer layer in the wear scars has been observed directly with micro laser Raman spectroscopy, which showed that in some cases the layer has a disordered graphite structure, different from the structure of the original DLC film [9,11]. Raman spectra also revealed evidence of graphitization of the DLC films in the wear track.

Due to the gradual formation of the transfer layer the friction coefficient of DLC can often change during a prolonged tribological test: it usually decreases during an initial break-in period, when the transfer layer is formed, then reaches a constant reduced friction stage [11,12]. A further reduction in friction was sometimes observed during measurements of long duration. This reduction was attributed to the complete transformation of the diamondlike to graphitelike carbon by a friction induced annealing [9]. A similar break-in stage from $\mu=0.4$ to $\mu=0.1-0.2$ was observed for nitrogen containing non-hydrogenated taC films, followed, however, by a gradual increase of the friction coefficients to 0.25-0.30 [13].

C. THE EFFECT OF HYDROGEN, OXYGEN AND WATER.

The transfer layer thus has a lubricating effect and its formation can be enhanced by hydrogen, but may be restricted in the presence of water or oxygen. The experimental evidence shows that, with the exception of hydrogen, adsorbed atoms and molecules, which lower the friction coefficients of diamond-diamond couples, usually increase the friction coefficient of DLC-DLC couples. Hydrogen passivates the dangling bonds in the hydrogenated DLC films and permits only weak interactions between DLC and the sliding partner. When hydrogen is removed from hydrogenated DLC, the formed dangling bonds cause strong interactions between the surfaces in contact, resulting in increased friction in UHV or dry nitrogen ($\mu=0.68$ [6]), similar to that reported for both graphite and diamond [8,14]. It has been observed that several different DLC

films, all having a friction coefficient of about 0.15 in ambient air, had ultralow friction coefficients of about 0.02 in UHV if their hydrogen content was more than 40 % [15], but had a friction coefficient of about 0.6 in UHV if their hydrogen content was below 34%.

The friction coefficients of two films with different hydrogen contents were recently studied in ultrahigh vacuum and in an atmosphere of pure hydrogen [16]. A high steady-state friction in UHV ($\mu=0.6$) was observed for the mostly sp^2 -bonded film of low hydrogen content, while super low steady-state friction ($\mu=0.002$) was observed for the film with the high hydrogen content in UHV and for the film with low hydrogen content in an atmosphere of hydrogen at 1 kPa. The super low friction was attributed to a hydrogen saturation across the shearing plane resulting in weak van der Waals interactions between the polymerlike hydrocarbon interface layers. Such a regime can be obtained either if the DLC film contains enough hydrogen incorporated during film deposition, or if hydrogen is present in the surrounding ambience during friction.

Water and oxygen at low pressures were found to have different effects on the friction of PECVD hydrogenated DLC [17]. Opposite to the expected, dry oxygen at pressure up to 6 kPa had no effect on the friction coefficient which maintained its UHV value of about 0.01. Surface spectroscopy revealed that triboxydation of the DLC film did not take place in the friction track. In contrast to the behavior in dry oxygen a friction threshold was observed in water vapors at pressures in the range of 0.01 kPa - 0.05 kPa, corresponding to relative humidities $RH=0.4\% - 2\%$. At $RH<0.4\%$ the friction coefficient maintained its ultralow UHV value, however at $RH>2\%$ the friction coefficient increased to values above 0.1 [17]. Considering that this range of relative humidity is difficult to qualify precisely, the strong change of friction regime at these relative humidities may explain the wide range of friction coefficients, from 0.01 to >0.1 , reported in the literature for so called "dry" ambient conditions.

D. MODIFIED AND NON-HYDROGENATED DLC

Certain applications may require the modification of DLC to preserve its wear resistance while changing its other characteristics, such as increase electrical conductivity or reduce surface energy. Incorporation of F or Si increase the contact angle of water to the films [18], yet F and Si containing DLC films can be prepared to be as wear resistant as the pure hydrogenated DLC [19, 20]. It has been reported that incorporation of Si in DLC reduces its friction coefficient [21] and that it renders the friction against steel insensitive to moisture [22,23]. However the incorporation of Si in DLC can also reduce its wear resistance, as much as 4 times [23]. The effect of Si on the friction coefficient of the films was found to be strongly affected by the counterface in the friction test. Metal containing DLC films have been found to reduce friction and wear both in sliding and in vibrating contacts for a broad range of testing conditions [24]. Nitrogen containing DLC (CN_x) films are characterized by friction coefficient and frictional behavior similar to regular DLC [4, 25].

The friction of the non-hydrogenated taC is much less investigated as compared to the hydrogenated DLC. Friction coefficients in the range of 0.10-0.15 at $RH=50\%$ have been reported for some taC films [25]. Friction coefficients at $RH=50\%$ of taC films deposited by a filtered cathodic vacuum arc have been reported to correlate to the sp^3 fraction in the films, reaching values down to 0.08 for the highest sp^3 fraction [26]. Films prepared by pulsed laser

deposition (PLD) have been found to have higher friction coefficients in a vacuum of 10 Pa than in dry nitrogen [28]. In air, the friction coefficient of the same films decreased with increasing relative humidity due to a sp^3 to sp^2 phase transition in the wear tracks on the taC film surface. The formation of a graphitic phase explained the humidity sensitive lubricating behavior of the hydrogen free a-C films in ambient environments and the increase in the friction coefficient in high vacuum conditions [28]. Similar to DLC films, a break-in stage has been observed in the friction testing of taC against sapphire ball [29]. The friction coefficient dropped from 0.5 to 0.1 during this stage indicating the formation of a transfer layer, similar to that observed in DLC films. Friction coefficients in the range of 0.10-0.12 at a relative humidity of 40 %-60 % were observed for the N containing taC films prepared by ion beam assisted deposition (IBAD) [30].

E. CONCLUSION

The friction coefficients of diamondlike carbon fields span a large range of values which depend on the properties of the films, as determined by the deposition system, and on the testing conditions. Of the testing conditions, the effect of testing ambience is best understood for the hydrogenated DLC.

In ambient air the hydrogenated DLC display friction coefficients of 0.1-0.4. The friction coefficients drop to values as low as 0.002 in UHV if the films contain large concentrations of hydrogen and attain similar values in a pure hydrogen ambience. Water vapors at a relative humidity as low as 0.4% change the friction coefficients from the ultralow values to the values in ambient air.

Non hydrogenated diamondlike carbon films have similar coefficients of friction in ambient air, but their friction in a different ambience has yet to be investigated.

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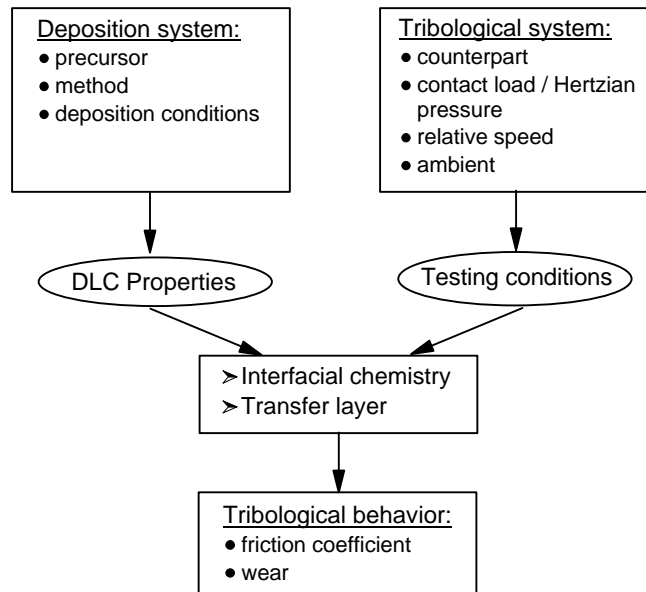


FIGURE 1. Schematic representation of the relationship among the friction coefficient of DLC films, their preparation conditions and tribotesting environment.