TOWARDS THE SOLID LUBRICATION OF SPACE MECHANISMS BY DIAMOND-LIKE CARBON COATINGS

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ABSTRACT

Diamond Like Carbon (DLC) has been studied for many years as a wear-resistant material with low friction coefficient. The film structure and properties strongly depend on the technique used for the deposition of the films. In recent years, new variations of DLC films, with various dopings, and new deposition procedures have been investigated. From an updated review of the tribological behavior of DLC, the present paper proposes a complete methodology to identify reproducible deposition conditions of carbon based functionnally gradient films to lubricate a space mechanism (gears, ball bearings). Ti / Ti-C:H / a-C:H films have been deposited by the hybrid technique of magnetron sputtering and d.c. plasma-enhanced chemical vapor deposition in various conditions. Analytical characterizations coupled with tribological tests have been performed to identify relationships between the deposition conditions, the film composition and properties, together with the tribological behavior in various environmental configurations. The present series of films exhibits a wide range of tribological behavior, with friction coefficient values in UHV ranging from less than 0.01 to more than 0.5 and with various wear rates under air or UHV. Typical DLC structures and compositions allowing the achievement of extremely low friction in vacuum and good behavior under air with low emissions of wear particles are identified and discussed. The next steps will consist in tribological life-tests and tests on mechanisms and components (gears, bearings...) lubricated with the best coatings.

1. INTRODUCTION

Many critical systems in spacecrafts or vacuum technology involve relative motion of contacting surfaces. Most of the applications require low and stable friction and low wear rates, taking into account the need of low power consumption, extreme reliability and precision of the mechanisms in a wide range of environments **[1-3]**. In particular, space mechanisms are required to function in vacuum, but also during the assembly, test, and storage phases which are often performed in the ambient atmosphere **[4]**. In addition, reliable data based on experimental investigations on the vibrational effects during the launching, the air-to-vacuum transition from the ground to the orbit, the effect of periodic temperature variations, the action of molecular or atomic beams and particles are not completely taken into account. The most common solid film lubricants are based on MoS_2 and Teflon. Sputter-deposited MoS_2 films are particularly sensitive to moisture on the operating and storage environments **[2]**. Recent investigations on doped or ion-irradiated MoS_2 sputter-deposited films and multilayered materials show an increased resistance to severe environmental conditions and an increase of durability in rolling or sliding tests **[5-6]**. However, as claimed by Fleischauer **[2]**, ambient air remains an extreme environment for sputter-deposited MoS_2 films and MoS_2 lubricants in general, limiting the critical performances of many space mechanisms.

From the various kinds of solid lubricant coatings, it has been recently shown that hydrogenated diamond-like coatings (a-C:H) may exhibit ultralow friction in high vacuum conditions **[7]**. However a literature survey indicates that the control of friction and wear of carbon-based films strongly depends both on the environmental conditions and the nature of the coatings as determined by the deposition process **[7-8]**. Miyoshi *et al.* **[9]** have recently studied the friction and wear of a-DLC/Ti-Ti_xC_y-DLC functionally gradient nanocomposite coatings in humid air and ultrahigh vacuum. The investigated films exhibit severe wear with brittle fracture in both the a-DLC top layer and the Ti-Ti_xC_y-DLC underlayer in ultrahigh vacuum. The humid air environment provides preferable tribological performances, in terms of friction level and wear rates. The role of predeposition treatments prior to the DLC deposition is emphasized by the authors, since the use of DLC at high loads may be limited by the brittle nature and high compressive stresses of these films.

The aim of the present study is to identify deposition conditions of carbon-based functionally gradient coatings, to identify the relationships between the deposition conditions, the nature of the films and their friction behavior at relatively high contact pressures (in the GPa range) both in humid air and ultrahigh vacuum. The present paper exposes the first steps of a wide program whose final objective is to deposit carbon-based films on space components, such as bearings and gears.

2. EXPERIMENTAL

The diamondlike carbon-based functionally gradient coatings have been deposited on polished Z100CD17 (440C) stainless steel (for tribological tests) and silicon (for analytical characterizations) substrates, by the hybrid technique of magnetron sputtering and d.c. plasma enhanced chemical vapor deposition (PACVD) carried out in the same reactor. Samples have been cleaned by a bias etching at - 200 V for 10 minutes prior to film deposition. A thin titanium underlayer (200 nm thick) has been firstly deposited through the sputtering of the magnetron source target in an argon plasma. A negative d.c. bias is applied to the substrate holder to control the ion impact energy, while the applied current controls the ion flux. The different d.c. bias values are reported in **Table 1**. Then, acetylene, as hydrocarbon precursor, has been mixed gradually with argon to produce a reactive plasma, generated by the negative magnetron source and the positive plasma source, which in turn led to the deposition of a Ti:C-H gradient. The acetylene flow rate was tuned to obtain desired intensities of the optical emission of titanium in the plasma, which is decreasing with increasing acetylene flow rate. Finally, the diamond-like carbon based top-layer has been obtained by placing a removable shield in front of the magnetron source, in order to reduce titanium incorporation in the plasma, and by keeping all parameters constant. The substrate temperature during film deposition was systematically lower than 200°C. The thicknesses of the films deduced from SEM cross-sectional views are reported in **Table 1** with other film characteritics. The films have been characterized by Rutherford backscattering spectroscopy (RBS) and forward recoil elastic scattering (FRES) to determine the composition, and by Fourier-transform infrared (FTIR) spectroscopy to determine the nature of the CH bonds. The film thicknesses have been measured by cross sectional micrographs. The film densities have been estimated by combining the previous thickness values with the thicknesses deduced from RBS measurements (in $g.cm^{-2}$). FTIR spectroscopy has been performed in the attenuated total reflexion mode (ATR), with a germanium crystal in contact with the surface of the investigated films. The residual stress has been determined from the curvature induced in the silicon wafer by the deposited film. Friction tests have been performed at room temperature either in ambient air at relative humidity RH = 40 – 60 %, either in ultrahigh vacuum (UHV) at 10^{-8} Pa, with a reciprocating pin-on-flat configuration, a sliding speed of 1 mm/s and a maximum Hertzian contact pressure of 1 GPa. A limited number of 500 cycles has been performed to discriminate the set of films, depending on their deposition conditions. The coatings have been systematically deposited on the plane counterface, whatever the bias conditions. The films have been also deposited on the steel pin counterface at -35, -50, -70, -90, -110, -130, and -260 V to check if the tribological behavior depends or not on the deposition of the films on both counterfaces, in comparison to the deposition on the plane only. Each test has been performed several times in the same conditions to check the reproducibility

Dc bias (V)	*Thickness (µm)*	*Top layer composition* H at.%	*O at.%*	*Ti at.%*	*Density ($g.cm^{-3}$)*	*Stress (GPa)*	*Friction in UHV*	*Friction in ambient air*
-35	3.1	52	4	1	1.3	-0.3	0.02	0.26
-50	2.7	52	4	1	1.0	-0.4	0.01	0.23
-60	3.3	51	4	1	1.5	-0.6	0.01	0.20
-70	3.5	46	6	1	1.5	-0.6	0.02	0.17
-80	2.8	46	4	1	1.4	-0.7	0.02	0.14
-90	2.5	46	5	1	1.4	-0.8	0.01	0.23
-100	2.2	46	5	1	1.4	-0.9	0.68	-
-110	1.7	46	5	3	1.3	-1.0	0.51	0.11
-120	1.4	45	5	3	1.5	-1.1	0.63	-
-130	2.7	45	5	2	1.5	-0.8	0.61	-
-140	1.4	43	5	3	2.3	-1.3	0.61	-
-150	2.6	41	5	2	1.1	-0.9	0.73	-
-260	1.5	38	5	2	1.6	-1.6	0.66	-

Table 1 *- Composition, properties and steady-state friction of diamondlike carbon-based functionally gradient films. The composition values given here correspond to the top layer of the gradient coatings.*

of the measurements.

3. RESULTS

Fig. 1 shows the UHV steady-state friction coefficients of the series of films, versus the bias voltage. Ultralow friction coefficients (< 0.02) are obtained for films deposited at bias ranging between -35 and -90 V. Films deposited at higher absolute values of bias (from -100 to -260 V) exhibit high friction (> 0.4) generally associated with the complete and rapid wear of the coating. Black bars in **Fig. 1** are related to tests with the films deposited on both the plane and the pin, whereas gray bars are related to tests with uncoated pins. As seen on **Fig. 1**, the additional deposition of the film on the pin does not affect the steady-state friction level, in comparison to the film deposited only on the plane.

Fig. 2 shows in detail the evolution of the average friction coefficients in UHV, versus the number of

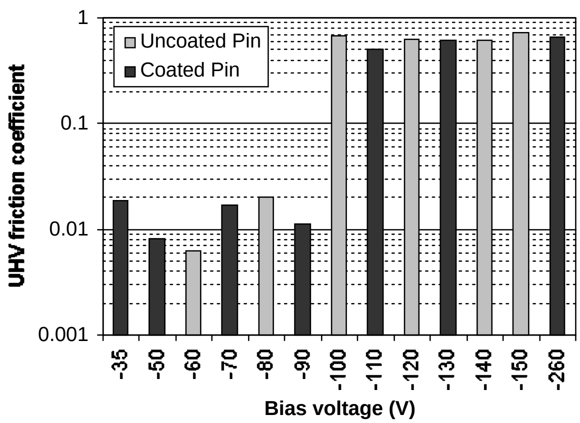

Figure 1: Steady-state friction of the films in UHV, versus the deposition bias.

sliding cycles, for the films deposited at -60 and -120 V respectively. Only the plane has been coated for both deposition conditions. Optical micrographs of the wear tracks at the end of the friction tests are shown inset. For the film deposited at -60 V, the friction coefficient starts from 0.13 during a short running-in period, before decreasing down to less than 0.01 till the end of the test. No significant production of wear particles is observed in the wear track of the plane, which remains difficult to visualize. Considering the limited number of sliding cycles, no quantification of the wear has been performed at the present stage of investigation. A transfer film with about the Hertzian diameter (50 µm) is observed on the initially uncoated steel pin counterface. For the film deposited at -120 V, high friction (> 0.4) is associated with the complete wear of the coating, the formation of numerous wear particles around both the wear track of the plane and the transfer film on the pin. The friction behavior versus sliding cycles of the film deposited at -60 V depicted in **Fig. 2** is similar to the friction behavior of the other films deposited at absolute bias values below 90 V. Moreover, within this bias range, no significant difference in the friction behavior versus sliding cycles has been observed when films were deposited both on the pin and the plane. In that case the short running-in period is also observed and a transfer film superimposed to the virgin film is seen on the coated pins at the end of the test. The friction tests in ambient air have been performed on the 6 films exhibiting ultralow friction in UHV (from -35 to -90 V). A similar test has been also carried out on the film deposited at -120 V exhibiting high friction in UHV. As reported in **Table 1**, friction coefficients in ambient air are ranging between 0.11 and 0.26, the highest values being obtained with films deposited at the lowest absolute bias, except the film deposited at -90 V exhibiting significantly higher friction (0.23) compared to the films deposited at -80 and -110 V. The other characterizations (**Table 1)** have been performed on the complete set of films to elucidate the origin of the friction threshold observed in UHV and the progressive evolution of the friction observed in ambient air. Depending on the deposition conditions, the total film thickness is ranging between 1.2 and 3.1 µm, including systematically a Ti underlayer of 0.2 µm deposited on the substrate by magnetron sputtering. The carbon-based layer deposited on the Ti underlayer is systematically constituted by Ti, C, H and O, with a Ti depth profile which should decrease from the interface with the previous underlayer towards the surface, considering the deposition procedure described previously. Indeed, RBS detects the presence of titanium up to the top surface, meaning that the shield in front of the magnetron source during the growth of the carbon-based films do not prevent the absence of Ti incorporation in the plasma. An average Ti concentration in the carbon-based layer ranging between 1 to 3 at.% has been deduced from RBS measurements, without more precise quantification of the Ti profile versus depth at the present stage of the study. XPS investigations (not shown) performed on the film deposited at -60 V, after etching to remove the extreme surface layers, indicate that the top layer of the functionally gradient film contains titanium oxide (Ti2p3/2 : 456-458 eV) but no titanium carbide (Ti2p3/2 : 455 eV) nor metal (Ti2p3/2 : 454 eV). This is confirmed by a C1s binding energy centered at 285 eV corresponding to usual values related to DLC **[11]**, without any signal at 281 eV related to TiC **[12]**. As seen by FRES experiments, the hydrogen content increases from 38 at.% to 52 at.% when the bias decreases in absolute value from -260 to -35 V (**Table 1**). **Fig. 3** shows FTIR spectra related to the films deposited at -60 and -120 V. The spectra, typical of hydrogenated DLC films **[13]**, display the stretching band around 2900 cm^{-1} related to sp^n CH_m (n, m = 1-3) (peak *a*), as well as the deformation peaks of sp^3 C-CH_3 at 1450 and 1370 cm^{-1} (peaks *b*). A stretch peak corresponding to conjugated aromatic sp^2 C=C carbon is also observed at 1600 cm^{-1} (peak *c*), but for the film deposited at -120 V, this peak is convoluted with a large

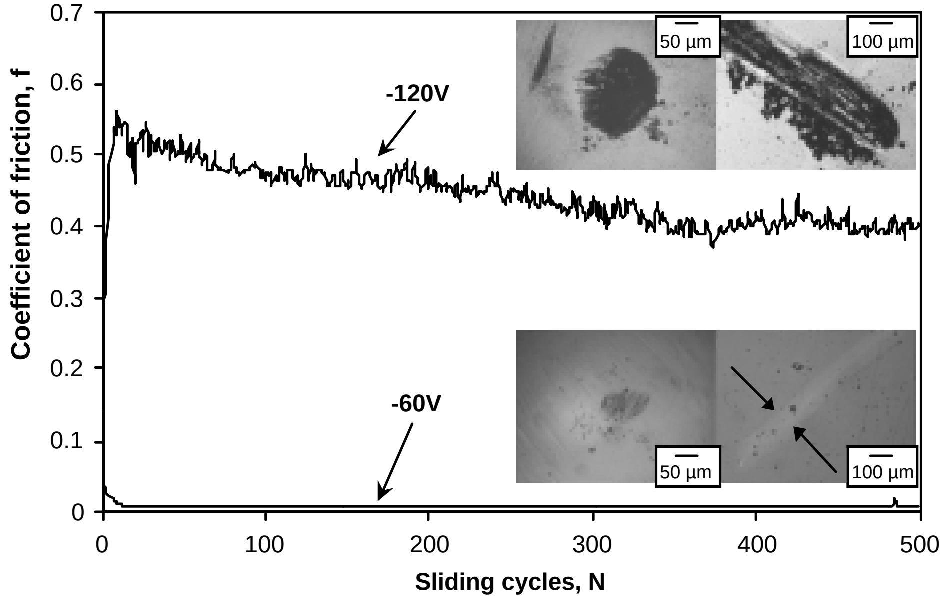

Figure 2: Friction coefficients in UHV, versus number of reciprcating sliding cycles, for the films deposited at -60 V and -120 V. Optical micrographs of the wear tracks of the pins (left) and on the planes (right) after 500 cycles are shown inset.

signal located above 1600 cm^{-1}, whose unambiguous interpretation remains unclear. The systematic comparison of the FTIR spectra related to the different films show that this large signal is identified only for films deposited at bias values ranging between -35 and -90 V (films exhibiting ultralow friction in UHV) and at the bias value of -100 V (lowest absolute bias related to the set of films with high friction). Consequently, for the investigated films, FTIR seems to provide an analytical signal which allows to discriminate the tribological behaviors in UHV, even if the origin of this signal remains uncertain. However the thickness probed by ATR-FTIR strongly depends on the optical properties of the film. As these properties were not investigated yet, the different spectra may not be related to the same thickness.

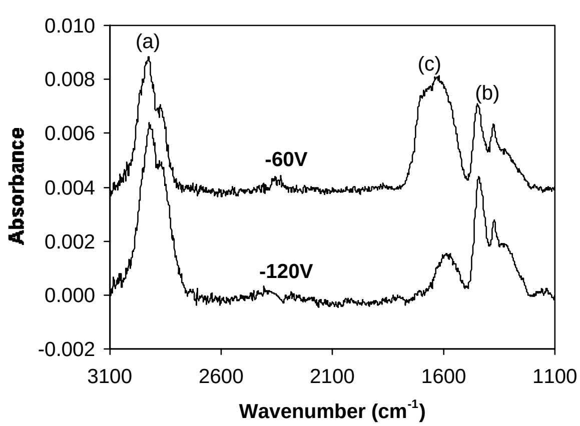

Figure 3: ATR-FTIR spectra related to the films deposited at -60 and -120 V (see text).

4. DISCUSSION

The present study confirms that the optimization of carbon-based films with low friction and long lifetimes at relatively high contact pressures in various environments requires both the presence of adaptative functionally gradient layers, intercalated between the substrate and the top DLC films allowing to achieve the design friction properties. This first step of the research program has been dedicated to identify deposition conditions allowing to achieve ultralow friction in UHV, being the first basic condition to go further in the optimization of carbon-based films for the solid lubrication of space mechanisms. Relationships between the deposition conditions and the film composition and properties are consistent with already published works, as reviewed in **[10]**. The PACVD deposition conditions of DLC films (precursor, electrical power, negative substrate bias, gas pressure and substrate temperature) cover large ranges of parameters. Species present in the plasma, both radicals and ions, are fragmented upon surface impact, after which the near-surface excited region is quenched by the underlying cold substrate. As reported by Robertson **[14]**, higher ion energy will increase the dehydrogenation and the compression of the growing film, thus leading to the various polymer-like, diamond-like and graphite-like carbon structures, depending on the deposition conditions. The properties of DLC films deposited by PACVD have been found to be a strong function of the energy of impacting ions which is related to the substrate bias (V_B) and pressure in reactor (P) by the relation **[15]** :

$$E \propto V_B / P^{1/2}.$$

Thus the properties of the films can be modified by adjusting the bias and/or pressure. For the reactor geometry, gas precursor and pressure used in the present study, an absolute bias increase from 35 to 260 V is associated to an increase of the dissociation of the precursor, thus leading to a decrease of the hydrogen content, as already observed [**7**]. The evolution of other investigated film properties (stress, density) reported in **Table 1** is more difficult to comment precisely. Obviously a higher dissociation of the precursor (i.e. higher bias) is known to increase the carbon network crosslinking, thus leading to higher density and compressive stresses [**10**]. The compressive stresses observed here follow this trend, with absolute values increasing from 0.3 GPa to 1.6 GPa with increasing biases. However, as reported in **Table 1**, the evolution of the density is difficult to comment precisely, since its dependence versus the bias is not perfectly regular. Probably the experimental uncertainty of thickness and RBS measurements coupled with rather reduced bias step increase are at the origin of the fluctuation observed. The friction behavior of amorphous carbon films depends on the deposition conditions and the tribotesting environment controlling tribochemical and graphitization effects, as recently reviewed **[7-8, 16-17]** on the basis of numerous publications. As generally observed on most of DLC coatings, the friction mechanism of the investigated carbon-based films is controlled by the build-up of a transfer film, followed by easy-shear within the interfacial material. The shearing ability strongly depends on the nature of the film and the surrounding gas present in the contact. A complete interpretation of the friction behavior of the present set of films would require the investigation of the structure and composition of the contact areas (transfer film, wear particles). Even if it has not been performed at the present stage of investigations, the general behavior observed in this study may be explained on the basis of previous considerations related to DLC films. Liu *et al.* **[18]** have shown that the steady-state low friction of DLC films (0.1 range) in ambient air is due to wear induced graphitization, *i.e.* formation of a low friction graphitized tribolayer. Thus, in ambient air, contrary to MoS_2 which undergoes tribo-oxidation strongly increasing wear, DLC generally undergoes tribo-graphitization. This may explain why the wear rates of DLC films can be extremely low **[19]** compared to MoS_2 in ambient humid air **[20]**, in spite of a friction level in the same range (0.1 – 0.2). This may represent a great advantage of the carbon-based films for solid lubrication of space mechanism, compared to MoS_2 films. The friction dependence of the films versus their hydrogen content in UHV and ambient air is a significant result of the present study. We have observed that the most hydrogenated films exhibit respectively significant lower friction (< 0.02) in UHV but higher friction (near or higher than 0.2) in ambient air, contrary to the less hydrogenated films tested in UHV (> 0.4) and in ambient air (near or lower than 0.15). If the friction variations versus the hydrogen content are rather progressive in ambient air (from 0.12 to 0.26, as measured on 7 of the 13 different films), the friction behavior of the complete set of films in UHV presents a surprising threshold observed near the bias values of -90 / -100 V, as reported in **Fig. 4**. A similar behavior has been already observed by others **[21]** and also by the authors of the present study on other DLC films **[7]**. The ultralow friction of smooth DLC layers in inert environments is attributed by Gardos **[22]** to the high surface finish and the presence of ultrathin hydrocarbon - polymer-like topcoats with weak Van Der Waals interactions (0.08 eV/bond) between hydrogenated carbonaceous chains. Therefore a higher hydrogen content may be associated with a higher contribution of the weak van der Waals interactions, whereas a lower hydrogen content is characteristic of carbon-based films whose friction level is similar to graphite in UHV. Indeed steady-state friction of graphite in the absence of any intercalant (inert environments) is high, consecutive to the overlapping of the π–π* orbitals (i.e. sub-bands of the graphite band structure) at selected sites of the Brillouin zone. Gardos indicates that the 0.4 - 0.8 eV binding energy between the basal planes is enough to render pristine highly oriented graphite a high friction material in UHV. A similar high friction behavior has been already observed on other DLC films with hydrogen contents lower than 34 at.%, the films being not completely worn in spite of high friction **[7]**. The results of the present study cannot be directly compared to **[7]**, since high friction cannot be attributed to the intrinsic friction behavior of the films containing less than 46 at.% of hydrogen, but to their rapid and complete wear. Nevertheless the existence of the threshold from high friction to ultralow friction tuned by the d.c. bias during deposition, coupled with the sudden vanishing of the FTIR wide band located above 1600 cm^{-1}, remains an interesting open question, which requires further investigations, as *in situ* characterizations of the transfer films.

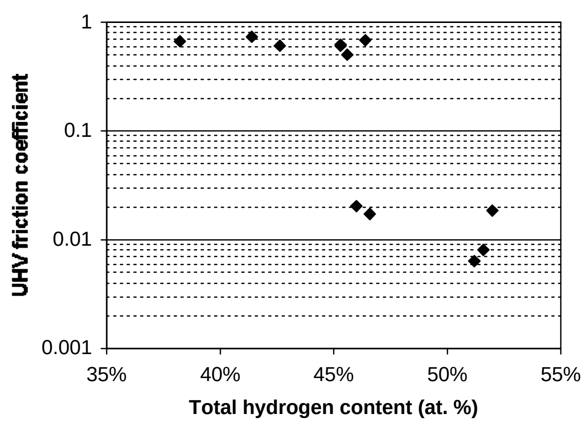

Figure 4: Steady-state friction in UHV versus hydrogen content of the films. Planes were coated. Deposition on the pins did not affect steady-state friction levels.

5. CONCLUSION

Diamondlike carbon-based functionally gradient Ti / Ti-C:H / a-C:H films have been deposited by the hybrid technique of magnetron sputtering and d.c. plasma-enhanced chemical vapor deposition, to identify deposition conditions exhibiting ultralow friction in UHV. From the variation of the bias during the film growth between -35 and -260 V, 13 different films have been deposited. Their structural investigations coupled with standardized friction tests in both UHV and ambient air indicate that amorphous carbon-based coatings exhibit a large range of friction behavior, depending on the deposition conditions. Indeed the films obtained at the lowest absolute bias values are more hydrogenated and exhibit steady-state friction coefficient below 0.02 in UHV, near 0.20 in ambient air. A sudden threshold between ultralow friction and high friction with severe wear is observed at d.c. bias values near -90 / -100 V. Higher absolute bias values lead to films exhibiting no wear resistance at all in UHV conditions. Consequently the potentiel use of diamondlike carbon-based functionally gradient films seems to be possible but requires careful design. The choice of the best carbonaceous films with their deposition process should be integral parts of the design of the lubricated device. If ultralow friction in UHV is achievable, further experiments are scheduled to quantify the endurance over long periods both in UHV and ambient air, and to understand more accurately the relationships between the nature of the films and their tribological behaviors.

AKNOWLDEGMENTS

The present study has been performed with the financial support of the Région Rhône-Alpes (France), which is acknowledged by the authors.

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