Tribological Behavior of DLC Films in Space and Automotive Oil under Boundary Lubrication

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Abstract: *The extremely hardness, high elastic modulus, excellent wear and corrosion resistance, high thermal and chemical stability, and the low-friction nature of the diamond-like carbon (DLC) coatings open further possibilities in improving tribological performance and reliability of different machine components. However, despite of the low friction coefficients normally observed for DLC-coated surfaces under dry sliding conditions, only a few DLC-coated tribological components are likely to be operated completely without a lubricant. In this paper, it was investigated the tribological behavior of DLC films in space and automotive oil under boundary lubrication. DLC films was grown over 316L stainless steel disks using plasma enhanced chemical vapor deposition. The tribological performance of the DLC film under Fomblin and 5W30 oil was investigated. Transferred materials on the DLC surface was examined using Raman Spectroscopy and contact angle. The combined effect of the transferred layer and the water content on oils might contribute to* *the effective improvement of the frictional and wear rate behaviors, which depends on the chemical structure and end groups in the lubricating oil.*

Keywords: Hybrid Lubrication, Wettability, Diamond-like Carbon, Aerospace and Industrial oil, Friction and Wear.

1. INTRODUCTION

Nowadays, the trends in the machine component industry are looking for higher performance, improving reliability and tolerances, more environment friendly products, less lubrication, and reduced frictional losses (Johnston et al, 2005). Owing to their attractive tribological properties, diamond-like carbon (DLC) coatings represent one of the means to achieve these goals (Rosado et al, 1997). The extremely hardness, high elastic modulus, excellent wear and corrosion resistance, high thermal and chemical stability, and low friction nature of DLC coatings make them good prospects for a wide range of space (Santos et al, 2006) and industrial components (Capote et al, 2008). Their expected life-time is very long and the film costs are normally very low compared to the component costs.

Depending on the deposition method, the deposition parameters, and surrounding environment, the dry sliding friction of DLC coatings against different metallic surfaces is typically reported to be in the range of 0.1-0.005 (Trava-Airoldi et al, 2007; Radi et al, 2008 and Liu et al, 1997). Despite of this favorable friction level, only a few DLC-coated machine components are likely to be operated without a lubricant, at least in the near future. This has many reasons. First, tribological properties of unlubricated DLC coatings are greatly influenced by the surrounding atmospheric conditions, especially the relative humidity (Liu et al, 1997 and Ronkainen et al, 1998). Second, the lubricant also serves to perform other functions in the mechanical system, such as cooling and wear particles removal. And third, very often it is not economically viable and sometimes not even technically feasible to coat all components in the system. Thus, a majority of

DLC coated machine components will continue to be operated under lubricated conditions, and will initially use the same lubricants as originally developed for uncoated steel surfaces.

With the introduction of DLC coated surfaces in existing systems the major concern is the compatibility with existing lubricants (Kano et al, 2006). In this manuscript, it was investigated the tribological behavior of DLC films in space and automotive oil under boundary lubrication.

2. EXPERIMENTAL PROCEDURES

In this study, DLC films with 20% hydrogen concentration were deposited on 316L stainless steel disks by using pulsed-DC discharge under controlled conditions (Capote et al, 2008). The tribological tests were performed on 4 mm diameter 316L steel ball and 50 mm diameter 316L steel flat pairs with and without DLC films. The tribological tests were performed in Fomblin Y LVAC 06/6, Perfluoropolyether vacuum oil, and 5W30 commercial, Poly-Alpha-Olefin (PAO) synthetic oil – (SAE, 5W30 API SL/CF), at room temperature, see Tab. 1.

Table 1 – Oil Properties (Klamann, 1984; Del Pesco, 1993).

Properties	Fomblin	5W30
Density (20 °C) g/cm^3	1.88	0.84
Viscosity (40 °C) cSt	22	60

The friction and wear tests were carried out by using a UMT-CETR ball-on-disk tribometer in the rotational mode with constant linear sliding speed under 2N normal load during 3000 cycles. The tests were run five times for each pair combination. A new position on the ball/disk was used for each test, and the friction coefficients were collected from the steady-state region (Eryilmaz and Erdemir, 2007).

After the friction measurements, the ball wear rate was calculated automatically by WYKO Surface Profilers, NT1100.

2.1 Water Determination by Karl Fisher

A Karl Fisher titration was carried out on three samples of the mobile and the stationary phase. The instrument used was an 841 Titrando including titration cell and indicator electrode from Metrohm International. The chemicals used for these experiments were methylene chloride, stabilized Karl Fisher reagent, and diluents for stabilized Karl Fisher reagent. All these chemicals were obtained from Fisher Scientific.

2.2 Contact angle analysis

The contact angles of deionized water, Fomblin and 5W30 oil on the disk surface coated and uncoated with DLC film were measured with sessile drop method, using a Drop Shape Analysis System in atmospheric condition at room temperature at least five times for each sample before and after tests under oils and environment air. A droplet with a volume of 2.5μL was released onto the surface of the sample from a syringe needle.

2.3 Microstructure analysis of DLC films

The atomic arrangement of the films was analyzed using Raman scattering spectroscopy (Renishaw 2000 system) with an Ar^+-ion laser (λ = 514 nm) in backscattering geometry. The laser power on the sample was ~0.6 mW and the laser spot had 2.5 μm diameter. The Raman shift was calibrated in relation to the diamond peak at 1332 cm^{-1}. In order to evaluate the coating homogeneity, several measurements were performed from different areas of the coated samples before and after the tests. All measurements were carried out in air at room temperature.

3. RESULTS AND DISCUSSION

3.1 Friction and Wear under oils

The friction coefficient and wear rate after 3000 cycles under environmental air (23ºC± 30%RH), Fomblin, and 5W30 oil can be seen in the Fig. 1 (a). The friction coefficient of DLC/DLC pair tested in Fomblin oil increased 33% compared to the same pair under environmental air. However, when 5W30 oil was added, the friction coefficient was maintained at 0.09. The 316L/DLC showed decreasing of friction coefficient at 11% and 77% when Fomblin and 5W30 oil was added respectively, compared to the same pair under environmental air. The 316L/316L showed the same behavior. However, it decreased 55% and 40% to Fomblin and 5W30 oil respectively.

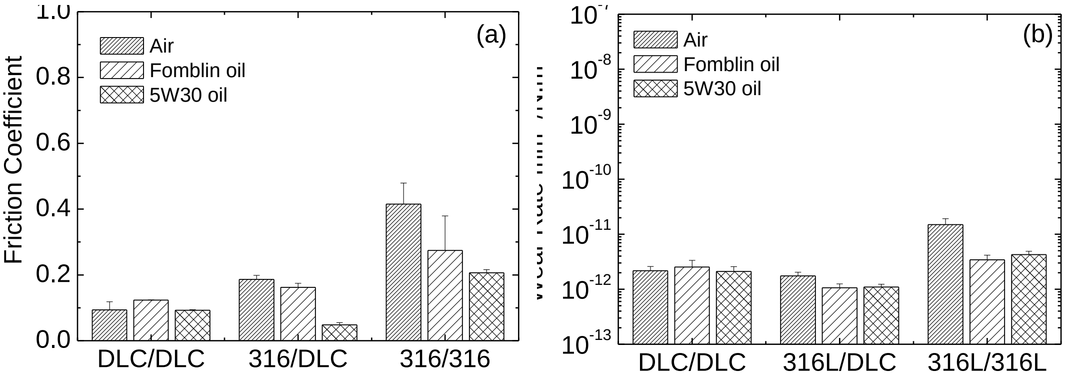

Fig. 1 - (a) Friction coefficient and (b) wear rate of DLC film under, environment air, Fomblin and 5W30 oil.

The results show that the wear rate is very low and almost the same for DLC/DLC pair after Fomblin and 5W30 oil added compared with environment air, see Fig.1(b). The wear rate was constant to 316L/DLC pair under Fomblin and 5W30 oil, but it decreased 39% in relation to environment air. The 316L/316L pair showed similar behavior, however, when Fomblin and 5W30 oil was added, the wear rate decreased 76% and 71% respectively.

3.2 Raman Scattering Spectroscopy

The Raman scattering spectra fitted using two Gaussian lines and their integrated intensity ratio of the D and G peaks (ID/IG-ratio) were compared. The DLC film of the present study before friction testes revealed similar ID/IG-ratio of 1.37 (Fig. 2 (a)). The spectra were fitted with Gaussian distributions associated with the peaks commonly found in amorphous hydrogenated carbon and labeled as G (graphite) and D (disordered), with band between 1100 and 1750 cm^{-1}, typical of amorphous hydrogenated carbon (Robertson and Ferrari, 2000). However, the Raman spectra obtained from the ball after friction from experiments in environment air, and oils showed some important and indicative changes. It is well known that the relative intensity of the D peak is related to the microcrystalline size of the graphitic cluster, where less-graphitic amorphous films have a lower ID/IG value (Scheibe et al, 1995). This transformation is strongly dependent on thermal and/or straining effects, as were observed and reported previously by others (Liu et al, 1996). DLC ID/IG ratio before and after tests under boundary-lubricated conditions can be seen in Tab. 2.

Table 2 - ID/IG ratio of DLC film before and after tests under boundary-lubricated conditions

	DLC (before)	Air	Fomblin oil	5W30 oil
ID/IG	1.37	1.72	1.56	1.08

Friction tests in environmental air, an additional T band centered at 1008.7 cm^{-1} was detected; see Fig 2 (b). It is a consequence of the 316L stainless steel wear, increasing ID/IG-ratio to 1.72. Researches confirm that the tribolayer is composed of wear particles from both 316L substrates, with the presence of CrNi and DLC films (Singer et al, 2000; Scharf et al, 2003). Friction tests with Fomblin revealed a decrease in ID/IG-ratio to 1.56 compared to tests in environmental air. It is also shown slight additional bands centered at 714.9 and 819.7 cm^{-1}, respectively that can be seen in Fig. 2(c). Meanwhile, after the friction tests under 5W30 oil, the Raman scattering spectroscopy of the sample showed two additional bands centered at 661.8 and

1834.5 cm^{-1}, respectively. Its ID/IG ratio decreased to 1.08. This can be related to the formation of a tribolayer scattered in the oil, see Fig. 2(d).

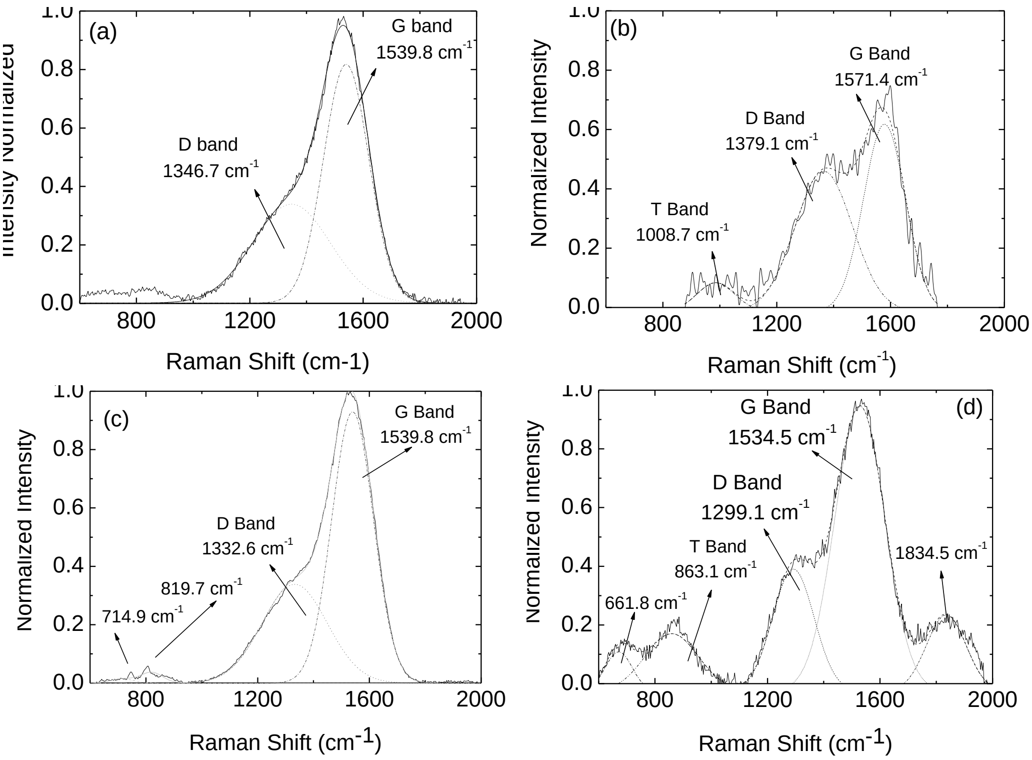

Fig. 2 - DLC film spectrums after tests under: (a) environment air, (b) Fomblin and (c) 5W30 synthetic oil.

3.3 Water Determination

Owing low water content in Fomblin oil, the coulometric Karl Fisher method was used. In this analyze methanol was used as solvent and vigorous homogenization of the solution was required. For 5W30 oil, became necessary to heat the oil until temperature 160ºC and N_2 as drag gas due to precipitation of Karl Fisher solution. The results showed in Table 3 are referent 30 ml of oil.

Table 3: Results obtained from coulometric titration method to Fomblin and 5W30 oil

Oils	**H_2O (ppm)**
Fomblin	6.4
5W30	952.4

3.4 Contact Angle

The wettability effect of water, Fomblin and 5W30 oil was examined on disks coated and uncoated with DLC film, see Fig. 3. The DLC film showed water contact angles around 80.5±0.5° and a minor variation was observed to Fomblin and 5W30 oil that presented 27.5±0.5° and 29.7±0.5° respectively. The 316L stainless steel surface showed water contact angles around 53.9±0.5° and same behavior was observed to Fomblin and 5W30 oil that presented 28.9±0.5° and 27.2±0.5°. However, the 5W30 oil showed better wettability in 316L steel surface meanwhile Fomblin showed similar behavior to DLC surface. It is interesting to note that under 5W30 oil, the 316L/DLC pair showed the lowest friction coefficient and wear rate while Fomblin showed good results of friction coefficient to DLC/DLC pair and 316L/DLC pair to wear rate.

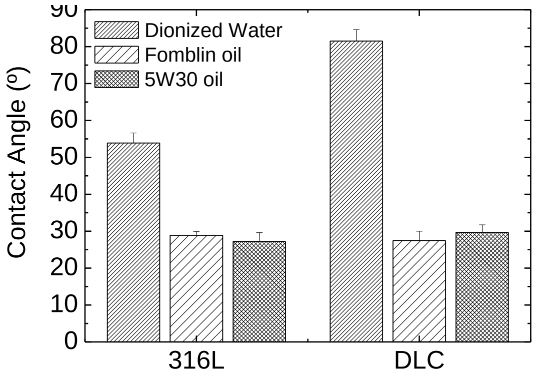

Fig. 3 – Contact angle of DLC coatings and 316L stainless steel.

It can be explained by dynamic behavior of the lubricant molecules on the DLC surface. Lubricant molecules having hydroxyl end groups adhere to the carbon at chain end via (1) hydrogen bonding with the hydroxyl end of the carbon surface, or (2) formation of a bona fide chemical bond reacted with a dangling bond shielded inside the carbon layer (Kasai, 2007; Tagawa et al, 2004). The hydrogen bonding is a weak interaction and it is constantly disrupted by the ambient thermal energy (Kasai, and Raman , 2006). It is well known that there are many polar functional groups on the DLC surface (Yanagisawa, 1994; 2001). There are many hydroxyl ends of lubricant molecules remaining intact on the carbon surface. At the open environment, the oil hydroxyl ends should seek to attain equilibrium interaction with polar components of the DLC film surface.

4. CONCLUSIONS

Tribological performance of the DLC film under Fomblin and 5W30 oil was investigated. Transferred materials on the DLC surface was examined using Raman Spectroscopy and contact angle. The main conclusions can be drawn as follows:

1) The combined effect of transferred layer and water content on oils might contribute to the effective improvement of the frictional and wear rate behaviors.
2) The amount of transferred layer of DLC film depends on the chemical structure and end groups in the lubricating oil.
3) Wettability behavior of the lubricant oil on the DLC surface is dependent on the hydroxyl end groups contained in these oils.

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