Effect of Refrigerant Gases (HFC134a and R600a) on the Tribological Behaviour of a Multifunctional DLC Coating

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Effect of Refrigerant Gases (HFC134a and HC600a) on the Tribological behaviour of a Multifunctional DLC Coating.

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ABSTRACT

Multifunctional DLC, Diamond-like Carbon coatings have been extensively studied and recognized as a promising solution to avoid wear and friction problems. However, the effect of the environment on the tribological behaviour, in particular in the refrigeration industry, is little studied yet. The present work aims to study the influence of refrigerant gases (HFC134a and R600a) on the tribological behaviour of multifunctional CrN-Si rich Diamond-like Carbon coatings, in particular on the tribo-chemical reactions. Tribological behaviour was evaluated using constant and incremental load reciprocating sliding tests. The constant load tests were conducted to access the friction coefficient and wear rates of specimen and counter-bodies whereas the incremental load tests (increments of 2 N at 15 min. intervals) allowed the assessment of the scuffing resistance of the coatings. The scuffing resistance was defined as the work (N.m) at which the value of the friction coefficient first rose above 0.20 (lubricity effect). The characterization of wear scars (tribolayers) was performed by optical interferometry, energy dispersive X-ray spectrometry associated with scanning electron microscopy, and micro Raman spectroscopy. It was verified a strong influence of the atmosphere via the formation of a tribolayer at the interface between body and counter body. This influence resulted in some disturbance of friction coefficient and contact resistance values. Tests performed in R600a atmosphere presented lower (36%) friction coefficient and lower (40%) scuffing resistance (surface durability) than those performed in HFC134a refrigerant gas. The observed differences were justified in terms of the tribo-chemical reaction between the multifunctional coating, the counter body and the refrigerant gases. Both results presented traces of Oxygen, but in the tests with HFC134a gas it was observed the presence of Fluorinated compounds in the tribo-layer. In the tests performed with R600a gas atmosphere it was found only carbon and Silicon, indicating different interactions of the environment. It is worth noting that these results can serve as a guide to the application: the low friction induced by the presence of R600a recommend it for applications where sustainability and energy saving are required while the use of HFC134a is recommended for applications requiring increased reliability (longer life).

1. INTRODUCTION

In the last years, academic and governmental entities have developed several projects in search for energy saving technologies. Many of these studies focused on surface engineering and related topics. In this context, surface
treatments and surface coating modifiers have faced the important challenge of reducing friction coefficient, wear losses and, consequently, energy consumption. For decades, the refrigeration industry has investigated and proposed various new technologies aiming energy consumption reduction. Only in the USA, Accordingly to United States Environmental Protection Agency, the refrigeration industry is responsible for approximately of 17.2% of the domestic energy consumption, and therefore plays a very important role in saving energy and natural resources.

In a refrigerator, the compressor is the main responsible for energy consumption and numerous emergent technologies are being studied and implemented each year. The great majority of compressors nowadays use fluid lubrication to reduce friction and wear. However, environmental factors suggest the reduction or even elimination of lubricating oils. In this sense, oil-less tribo systems represent a new challenge for surface science and engineering, stimulating new projects related to coatings and self-lubricant materials. According to Erdemir (2001), the development of advanced technology for coatings with low friction coefficient and high wear endurance became a high source of activities and researches around the world in the tribological field. Amorphous carbon coatings, known as diamond-like carbon (DLC), have been an alternative in many technological applications, such as hard coating for tools, automotive parts, computer hard drives and micro electro mechanical systems (MEMS). The applications are mainly associated with its high hardness, high chemical inertness and solid lubrication capacity Viana et al (2010). The low friction coefficients associated with Diamond-like Carbon coating is often associated with tribolayer formation, which is a result mainly of DLC transfer from to the counter body and vice versa Ronkainen et al (1996), Gril (1993), Lifang and Guang (2008), Erdemir et al (1995). The genesis of these tribo layers is strongly dependent on the environment. For atmospheres such as air, oxygen or nitrogen, the increase of humidity usually reduces the friction coefficient of Diamond-like Carbon-steel contacts Lifang and Guang (2008), Erdemir et al (1995). In a study performed by De Mello et al. (2009), it was shown that the presence of protective atmosphere (R600a) modifies the chemical structure of the tribolayer generated on the counter body, reducing the friction coefficient and the wear rate of the system (DLC / steel AISI 52100). In another work performed by Demas and Polycarpou (2006) pin-on-disc tests were performed with gray cast iron (pin and disc) without lubrication and different atmospheres (O₂, CO₂, N₂, Ar and R134a). Under O₂ atmosphere, the wear was ruled by the oxidation that occurs on the wear track, whereas in air and R134a it also contained an adhesive component. Under N₂ atmosphere, the wear was dominated by adhesion, while in CO₂ a slight polishing on the surface occurred, removing only the most prominent asperities, thus leading to the best tribological performance among the tested atmospheres. The settling of tribo layers on the real contact area rule the tribological behaviour of tribo systems. Their dimensions are reduced (nanometres), and this factor hinders to understand their formation and stabilization. Tribo layers are formed from physicochemical interactions between the surfaces in contact and relative motion, which ranges from mutual transfer of materials and reactions between atmosphere, lubricants and contaminants present in the contact Luo et al (2009). This work presents a surface treatment that has been used with great success in oil free hermetic compressors, consisting of a multi-functional coating composed of an outermost Diamond-like Carbon film applied onto a low Carbon steel substrate with an intermediate Chromium base layer used as a load bearing layer. The Diamond-like Carbon family consists of amorphous carbon hydrogenated alloys (a-C:H), as shown in the ternary diagram on Figure 1, where different families of DLC’s are characterized by the percentage of hybridizations sp², sp³ and amount of hydrogen Robertson (2002). In addition, doping elements can be incorporated into Diamond-like Carbon coatings to modify their properties, such as silicon (a-C:H:Si), which decreases the free energy and the residual stress of the coating, modifying its tribological behaviour Donnet (1998).

According to Bowden and Young (1951) the low friction coefficient of diamond films is due its inertness nature and/or passivation of contact interfaces. In this way, some researchers such as Miyake et al (1995), Smentkowski et al (1996, 1997) e Molian et al (1993) developed different routes for the surface passivation of Carbon films, adding different chemical elements to reach ultra low friction coefficients. Other studies investigated the presence of fluorine in the Diamond-like Carbon coatings to reduce friction coefficients and wear rates (Miyake et al, 1995, Smentkowski et al, 1996; Molian et al, 1993). Dugger et al (1992) showed that adsorbed gases at the contact interface have great influence on wear rates due to the bonding changes caused by those gases, De Mello et al (2009) showed the tribological behaviour of multi component Diamond-like Carbon coating in different refrigerant gases used by the refrigeration industry. They presented different friction coefficients and wear rates for each atmosphere including the influence of Oxygen contamination on tribological properties. The present study aims to identify the influence of two of the most used refrigerant gases in the refrigeration industry, HFC134a and HC600a refrigerant gases, on the frictional behaviour and wear of CrN-Si DLC multifunctional coatings.
2. MATERIALS AND METHODS

The multifunctional Diamond-like Carbon coating used in this work was a proprietary multifunctional Chromium base plus a DLC coating, where an intermediate layer composed of chromium nitride is responsible for the load bearing and an uppermost a-C:H layer deposited by PACVD (Plasma Assisted Vapour Deposition) is used as a self lubrication film. The substrate was an AISI 1020 low carbon steel. The aim of this configuration was to avoid the so called “egg shell effect”, which may cause coating spalling due differences in mechanical and physical properties of the Diamond-like Carbon layer (high hardness) and the soft substrate. The samples were polished prior to coating deposition in order to standardize the surfaces.

2.1 Tribological Evaluation

The tribological tests were conducted using a ball-on-flat contact geometry in a micro tribometer UMT-01 CETR under reciprocating sliding configuration, as indicated in Figure 2-a using two types of experiments:

i- Wear tests: Reciprocating sliding tests conducted at constant normal load to access the friction coefficients and wear rates of specimen and counter-bodies.

ii- Durability tests: Reciprocating sliding tests carried out using an incremental loading mode. The scuffing resistance was determined by increasing the normal load in increments of 2 N at every 15 min. (up to 91N, which was the limit of the load cell used in this test configuration). In this study, the scuffing resistance was defined as the work (N.m) at which the value of the friction coefficient first rose above 0.20 (lubricity effect) as proposed by De Melo and Binder, 2006 and illustrated in Figure 2-b.

In both types of experiments, a hard Si₃N₄ ball (diameter 2.381 mm) was fixed onto a pivoted arm and rested against the specimen surface, which moved at constant stroke (5 mm) and frequency (2 Hz). The ball surface was used in the as-received condition and a new surface region was used for each test. Contact potential and friction force were continually logged (acquisition rate of 1 Hz). The tests were conducted under controlled relative humidity (50 %) and temperature (22±2 °C). The results are the averages from, at least, five experiments for each analysed condition. Wear scars were analyzed by using SEM-EDX as well as FEG-SEM; micro Raman spectroscopy and white light interferometry.

Figure 1: Ternary phase diagram for hydrogenated amorphous carbon Robertson (2002).

Figure 2: a) Contact geometry. b) Scuffing test as proposed by De Mello and Binder, 2006.
A semi-hermetic chamber, Figure 3, was developed to vary the test environment (refrigerant gas atmospheres) and avoid humidity and air contamination. Light vacuum was performed before each test and slight positive pressure was assured during the whole tests by a constant flow of the refrigerant gases.

Figure 3: Semi-hermetic chamber.

The surface topography of the specimens before and after the tests was assessed using white light interferometer WYKO NT9000 and Vision software provided by Veeco®, which was used to obtain the topographic parameters, as well as measurements of wear volume of the Diamond-like Carbon coating samples, as exemplified in Figure 4.

Figure 4: a) 3D Topographic analysis; b) Profile of the wear scar.

The wear rates of counter-bodies were calculated measuring the wear cap diameter on the spheres using the volume of the removed material and the wear rate were calculated according to G99-95 ASTM (2010) assuming flatness of the cap.

2.2 Tribochemical Analysis

The characterization of the tribochemical layers in the wear tracks produced in the Diamond-like Carbon coatings and counter-bodies was performed using EDS mapping elementary analysis by energy dispersive spectrometer coupled to a SEM – Scanning Electron Microscope, and Raman scattering spectroscopy using a Renishaw - InVia Raman Microscope system with an Ar+ ion laser (λ=514 nm). Recent studies showed that Raman scattering spectroscopy is a powerful and safe methodology to characterize Diamond-like Carbon films, which presents two bands in the 800 - 2000 cm⁻¹ range. The D band centred at 1360 cm⁻¹ and the G band at 1560 cm⁻¹. In amorphous carbon the I_D/I_G index is measured to identify the size of the sp² phase organized in rings. If I_D/I_G is negligible, the sp² phase is mainly organized in chains, or, even if rings are present, the π bonds are not fully delocalized on the rings Staturi et al (2009), Cassiraghi et al (2005a). Hydrogen content indicates the density of sp³ fraction in the bonding parameters of Diamond-like Carbon films. The ratio between the slope, m, of the fitted linear background and the intensity of the G peak, m/I(G), can be empirically...
used as a measure of the bonded H content Cassiraghi et al (2005b). The calculation of H content follows the equation (Casiragui et al, 2005):

\[
H(\text{at}%) = 21.7 + \log \left( \frac{m}{t(G)} [\mu m] \right)
\]  

(1)

3. RESULTS

Figure 5-a presents the typical aspect of the multifunctional coatings. The cross section clearly shows the presence of the columnar Chromium base layer and the uppermost Si rich a-C:H.

The deposition process had little influence on surface topography, since the grinding marks before deposition were still visible, as indicated by the arrows in Figure 5-b. In fact, the grinding marks were still present, and even more evident, within the wear scars.

![Figure 5: Typical aspects of the multifunctional coating. a) Cross section. b) Wear scar (top view)](image)

Figure 6-a presents the effect of the different atmospheres on the evolution of friction coefficient with sliding distance and applied normal load.

![Figure 6: Durability tests. a) Evolution of friction coefficient with sliding distance and applied normal load.; b) Surface durability.](image)

There is a transient associated with the onset of contact between specimen and counter-body at the beginning of tests before a steady state is reached. It is reasonable to suppose that the stabilisation of the friction coefficient after the
Transient is related to the generation of a protective tribolayer, where the transient corresponds to the kinetics of formation of the layer. As long as the formation rate of the tribolayer is different from the degradation rate, friction coefficient will vary. Once this formation rate is equal to or greater than the degradation rate, a steady state is reached (Balu, 2005, Balu, 2009). The tribological tests performed with refrigerant gas R600a presented lower average steady state friction coefficient when compared to those obtained in the tests using R134a, Figure 6-a. However, in R134a atmosphere the multifunctional coatings presented higher durability (approximately 40%), Figure 6-b. It is worth noting that the R600a tests were interrupted when the coatings collapsed (µ≥0.2), whereas the tests conducted in R134a were finalized only when the maximum load supported by the tribometer was applied.

A synthesis of the tribological behaviour (constant loads wear tests) is presented in Figure 7. It is possible to identify different results for each refrigerant gas for all parameters analyzed: friction coefficient, specimen wear rate and counter-body wear rate. Although the tests performed with R134a gas showed a higher friction coefficient (36%), they presented lower wear rates for both specimens (50%) and counter-bodies (one order of magnitude) than those conducted in R600a. In order to understand the differences in tribological behaviour the wear scars present on the specimens and counter bodies were analysed by micro-Raman spectroscopy (Figure 8). The differences between the peak positions of the Raman spectra for the specimen wear scars are not significant, Figure 8-a and Figure 8-c. They present two typical DLC broad peaks (G-band at approximately 1572±12 cm\(^{-1}\) and D-band at 1360±5 cm\(^{-1}\)). However, the intensity ratio of the D-band to G-band, \(I_D/I_G\) (\(I_D/I_G134a=0.92±0.04\); \(I_D/I_GR600a=0.39±0.02\)), as well as the hydrogen content (\(H%_{134a}=33±4\) H%\(_{R600a}=22±4\)) varies according to the atmosphere indicating tribochemical reaction of the specimens with the surrounding atmosphere. It is also noticeable that, for the case of the tests conducted under R600a environment, the spectra of the tribo layers presented in the wear scars of the specimens (Figure 8-c) or in the counter-bodies (Figure 8-d) are almost identical and indicate the beneficial presence of Diamond-like Carbon coating on both sides of the tribo pair. In this sense, the transfer of Diamond-like Carbon film to the counter-body may contribute for its consumption and its higher wear rate when compared to those presented by the tests conducted under R134a environment.
On the contrary, the spectra found in the wear track of the tests in R134a atmosphere changed according to their position in the tribo pair. In the wear scar, the spectra were similar to those found in the previous case with R600a, Figure 8-a, whereas those found in the wear marks of the counter bodies were radically different, Figure 8-b. The spectra presented smaller bands at lower frequencies. The positions of the bands match fairly well those observed for iron oxide phases De mello et al (2009) and their origin can be attributed to the formation of iron oxide by tribochemical reaction of the counter body with the surrounding and is, probably, a consequence of the high energy availability associated with high friction coefficients. Sei J. Oh et al (1998), Ouyang et al (1995a,1997b), Scharf et al (2003), De Mello et al (2009). It is reasonable to suppose that the presence of iron oxides is likely to induce higher friction coefficient. Figure 9 shows the typical SEM and elemental mapping images of the specimen wear scar for samples tested under R134a and R600a atmospheres. It is clearly visible that there was material transfer between specimen and counter-body as well as tribochemical reactions with the surrounding atmosphere. Oxygen was found on both wear scars, as determined by the distribution map of this element indicating a contamination of the chamber. In a recent paper, Barbosa et al (2015) clearly evidenced that this contamination originates from the refrigerant gases, in particular R134a. For the tests conducted under R134a atmosphere it is noticeable the presence of fluorine as indicated in the correspondent elemental map. Fluorine is adsorbed onto the surface of Diamond-like Carbon coating, forming a passivation layer with low friction coefficient and wear explaining the superior tribological performance for the tests under R134a environment. Indeed, some researchers such as Smentkowski et al (1996) and Molian (1993) developed effective ways to passivate these films, incorporating fluorine into the Diamond-like Carbon coating in the deposition step.

Figure 8 - Raman spectra. a) Specimen, R134a. b) Counter-body, R134a. c) Specimen, R600a. d) Counter-body, R600a.

On the other hand, the EDS elemental mapping analysis of the wear marks produced with R600a, Figure 10-b,
presented carbon, silicon and oxygen, indicating only contamination of the test chamber with air.

**CONCLUDING REMARKS**

1. The surrounding atmosphere had a strong influence on the tribological behaviour of the multifunctional coating.
2. In R134a atmosphere the multifunctional coatings presented higher scuffing resistance for this experiment (approximately 40%). The tests performed with R134a gas although presenting a higher friction coefficient (36%) presented higher wear rate for both specimens (50%) bodies and counter-bodies (one order of magnitude) than those conducted in R600a.
3. For the case of the tests conducted under R600a environment the spectra of tribo layers in the wear scars of the specimens and in the counter-bodies are almost identical and indicate the beneficial presence of Diamond-like Carbon films on both sides of the tribo pair.
4. On the contrary, the spectra found in the wear track of the tests in R134a atmosphere changed according to their position in the tribo pair. Spectra found in wear marks of the counter bodies were radically different: They presented smaller bands at lower frequencies which were attributed to the formation of iron oxide by tribochemical reaction of the counter body with the surrounding.
5. In tests performed in an R134-a atmosphere, fluorine is adsorbed on the surface of Diamond-like Carbon coating, forming a passivation layer with low coefficient of friction and wear, explaining the superior tribological performance of the R134a tests.

![Figure 9: Elemental mapping of wear scars. a) R134a. b) R600a.](image)

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