EFFECT OF REFRIGERANT GASES ON THE TRIBOLOGICAL BEHAVIOR OF A CrN-SiDLC MULTIFUNCTIONAL COATING APPLIED TO SOFT SUBSTRATE[1]

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Abstract

DLC 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 behavior is little studied yet. The present study aims to analyze the tribological behavior of DLC coatings in refrigerant gases HFC134a and HC600a used by refrigeration industry, in particular the tribo-chemical reactions. Tests performed in HFC134a atmosphere presented higher friction coefficient and durability than those performed in HC600a refrigerant gas. The differences observed were justified in terms of the tribo-chemical reaction between DLC 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 on the tribo-layer. In the tests performed in HC600a gas atmosphere it was found only Carbon and Silicon indicating different interactions of the environment.

Key words: Wear; Tribolayer; DLC; Tribochemical.

EFEITO DE GASES REFRIGERANTES NO COMPORTAMENTO TRIBOLÓGICO DE UM REVESTIMENTO MULTIFUNCIONAL CrN-SiDLC APLICADO A SUBSTRATOS MOLES

Resumo

Revestimentos de DLC vêm sendo extensivamente estudados e reconhecidos como uma solução promissora para evitar problemas de atrito e desgaste. Entretanto, o efeito da atmosfera no comportamento tribológico é ainda pouco estudado. O presente estudo visa analisar o comportamento tribológico de revestimentos de DLC com gases refrigerantes HFC134a e HC600a utilizados pela industria de refrigeração, em particular as reações tribo-químicas envolvidas nestas atmosferas. Testes realizados em atmosfera de gás HFC134a apresentaram coeficiente de atrito e durabilidade maiores que os testes com gás refrigerante HC600a. As diferenças observadas foram justificadas em função de reações tribo-químicas entre o revestimento de DLC, contracorpo e gases refrigerantes. Ambos os resultados apresentaram traços de Oxigênio, mas nos testes com o gás HFC134a foi observado a presença de compostos Fluorados na tribocamada. Nos testes realizados em atmosfera de HC600a foram encontrados apenas Carbono e Silício, indicando deferentes interações com o ambiente.

Palavras-chave: Desgaste; Atrito; Tribocamada; DLC;Reações tribo-químicas.

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1 INTRODUCTION

In the modern industry there are several kinds of applications for hard coatings especially for carbon-based coatings in order to avoid wear or reduce friction problems.(1)

Most part of coating applications are in hardened metals, alloyed steels and tool steels increasing the cost of manufacturing and finishing processes. Even though soft metals are easier to manufacture and cheaper than alloyed steels, they normally do not present high performance as mechanical support to hard coatings.

Several researchers had studied the contamination of the tribological interface (tribolayer) of carbon-based films. They verified that when these coatings are used in very clean, high vacuum and high temperature, the coefficient of friction and wear rate are higher than in no controlled environments. They attributed this behavior to the contaminants present on the tribolayer which are mechanically dissociated and removed from the interfaces being related to the uncompleted bonding of the tribolayer structure.(2-5)

Other studies investigated the presence of Fluorine in the DLC coatings to reduce the coefficient of friction and wear rates.(6-8) Dugger, Peebles and Pope(4) showed that adsorbed gases at the contact interface have great influence in the friction and wear due the bonding changes associated with the gas during frictional evaluations. When a specific atmosphere of gases and or air contamination are present on tribological tests of the DLC coatings the results are completely changed, indicating tribochemical reaction between DLC, counter-body and atmosphere.

Mello et al.(9) have showed the tribological behavior of multi component DLC coating tested in different refrigerant gases used by the refrigeration industry. They presented different behavior of coefficient of friction and wear rates according to the atmosphere, especially at the presence of Oxygen contamination, corroborating previous studies.

The present study aims to identify the influence of HFC134a and HC600a refrigerant gases on the frictional behavior and wear of CrN-SiDLC multifunctional coating.

2 Experimental Methods

The tribological tests were conducted in a ball-on-flat contact geometry, using a micro tribometer UMT-01 CETR in a reciprocating sliding configuration, as indicated on figure 1a. During the tribological tests, coefficient of friction, normal load, friction force and test time were controlled and stored.

The counter-body was a 4.762 mm diameter Si_3N_4 ball and Hertzian contact stress of 1.97 GPa. The ball surface was used in the as-received condition and a new surface region was used for each test.

Two kinds of unlubricated tribological tests were conducted: durability test and wear tests with constant normal load.

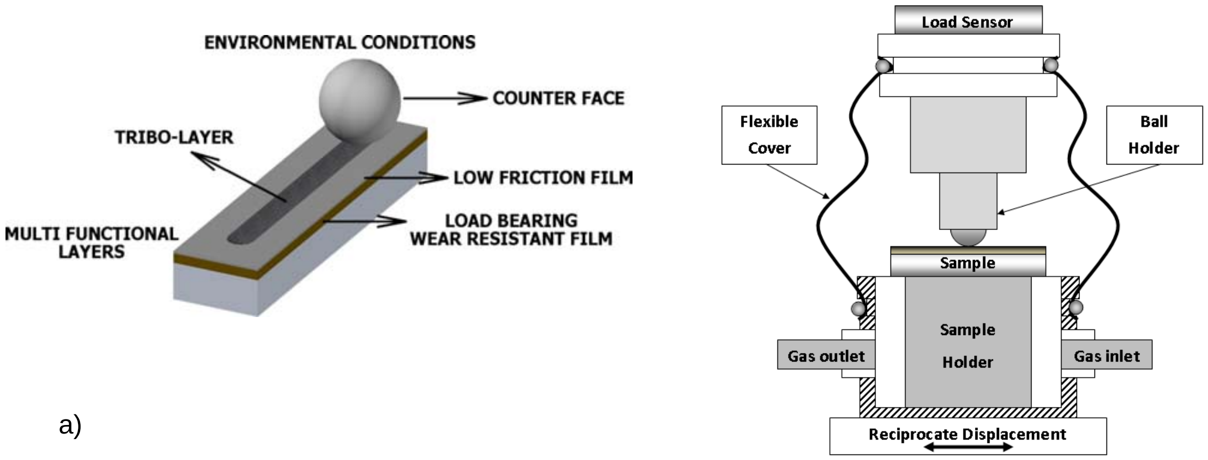
The durability tests were performed using the methodology proposed by Mello and Binder(10) where the normal loads are applied in several steps of time and the coefficient of friction and sliding distance is monitored for posterior analysis. These tests were conducted to establish the coating critical load. The normal load was incremented in 2 N at an interval of every 15 minutes. In this study, the tribolayer durability was defined as the work (N.m) which the value of the friction coefficient first rose above 0.20 (lubricity effect).

The wear tests were performed to determine the wear rate of DLC coating in different gases atmospheres. The duration of the tests was one hour. The wear rates were calculated considering the volumetric amount of material removed in each part: Sample (DLC coating) and counter-body (Si_3N_4 balls).

A semi-hermetic chamber (Figure 1b), was developed in order to use the refrigerant gases and avoid humidity and air contamination. Light vacuum were performed before tests and a gas flow with the respectively gases were assured during the whole tests.

Topographic parameters were controlled using white light interferometer WYKO NT9000 and Vision software provided by Veeco®, which was used to obtain the topographical data and the measurements of wear volume of the DLC samples.

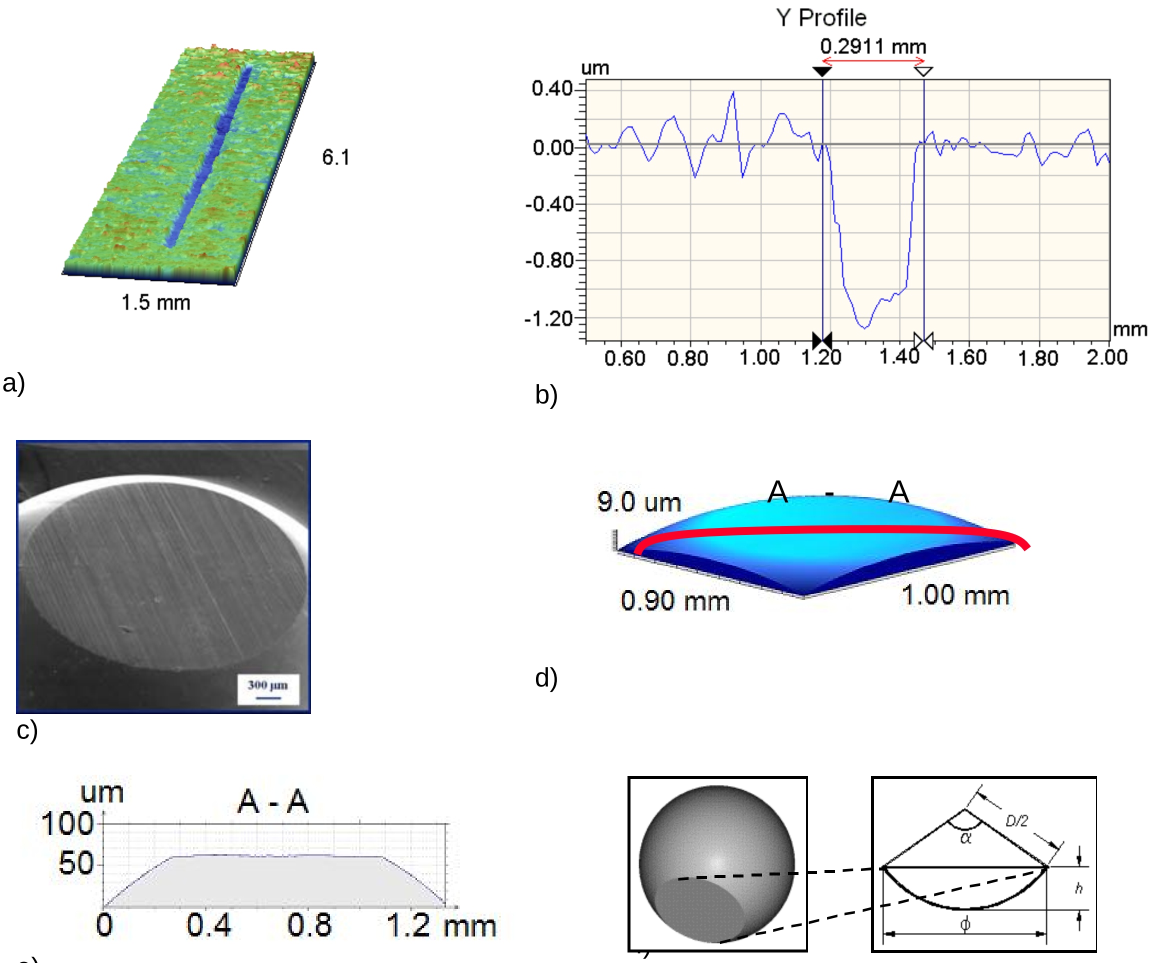
The wear rate of counter-body was calculated measuring the wear cap diameter on the spheres using the method illustrated on Figure 2, where the volume of the removed material and the wear rate were calculated according to G99-95 ASTM(11) assuming flatness of the cap.



a)

b)

Figure 1: a) Contact geometry; b) Semi-hermetic chamber.



a)

b)

c)

d)

e)

Figure 2: a) Topographic analysis of wear scar; b) Wear scar profile; c) Sphere cap image; d) Optical measurement; e) Image analysis system; f) Sphere cap volume.(12)

$$Vol = \left(\frac{\pi . h}{6}\right) . \left[\frac{3}{4} \text{Ø}^2 + h^2\right] \quad \text{Eq. 1}$$

$$h = \frac{\phi}{2} tg\left(\frac{\alpha}{2}\right) \quad \text{Eq. 2}$$

$$\alpha = 2.a\,\mathrm{sen}\left(\phi^2 / D\right) \quad \text{Eq. 3}$$

Where:
Ø = wear scar diameter, and
h = sphere cap high
D = ball diameter

The DLC coating used was a proprietary multifunctional CrN-SiDLC. A base layer composed by Chromium Nitride, 3.8 µm thick, plays the role of a mechanical support layer and a-C:H, 1.8 µm thick deposited by PACVD, is used as self lubrication coating. The substrate was a grinded and polished low carbon steel AISI 1020. The aim of this configuration is to avoid the so called “egg shell effect”, that causes the coating fragmentation due the differences between hardness of the DLC coating (high hardness) of the soft substrate (low hardness).Chemical characterizations of the DLC coating and counter bodies were done by EDX mapping elementary analysis coupled to a SEM - Phillips XL30 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 safe methodology to characterize DLC films, which presents two bands in the 800 – 2000 cm^{-1} range. D band centered at 1360 cm^{-1} and G band at 1560 cm^{-1}. In amorphous carbons ID/IG index is measured to identify the size of the sp^2 phase organized in rings. If ID/IG is negligible, the sp^2 phase is mainly organized in chains, or, even if rings are present, the π bonds are not fully delocalized on the rings.(13-15)

Hydrogen content indicates the density of sp^3 fraction in the bonding parameters of DLC 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.(14) The calculation of H content follows the equation:

$$\mathrm{H}\ \ [\mathrm{at}\,\%] = 21.7 + 16.6\log\left\{\frac{m}{I(\mathrm{G})}[\mu\mathrm{m}]\right\}$$

Eq. 4

3 RESULTS

Figure 3a presents the effect of atmosphere on the evolution of friction coefficient with sliding distance and applied normal load.

The tribological tests performed with refrigerant gas HC600a presented lower coefficient of friction than the tests with HFC134a. However, in HFC134a atmosphere the coatings presented higher durability (approximately 40%). It is worth noting that the HC600a tests were interrupted when the coatings collapsed whereas the tests conducted in HFC134a were finalized only when the maximum load supported by the tribometer was applied.

The wear rate of the samples and counter bodies are presented on Figures 3c and 3d. Tests performed with HFC134a gas presented higher wear rate for both samples (50%) and counter-bodies (more than one order of magnitude) than those conducted in HC600a.

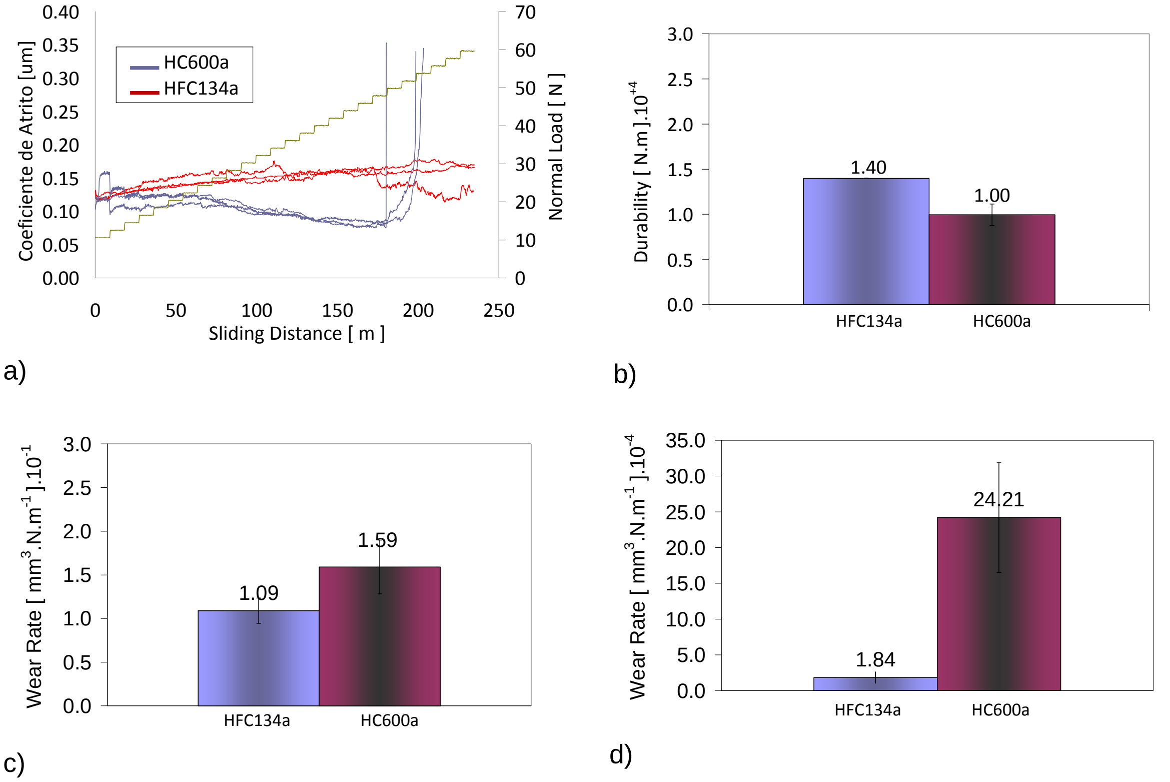


Figure 3 a) Durability tests; b) Durability comparison; c) Sample wear rate; d) Counter body wear rate.

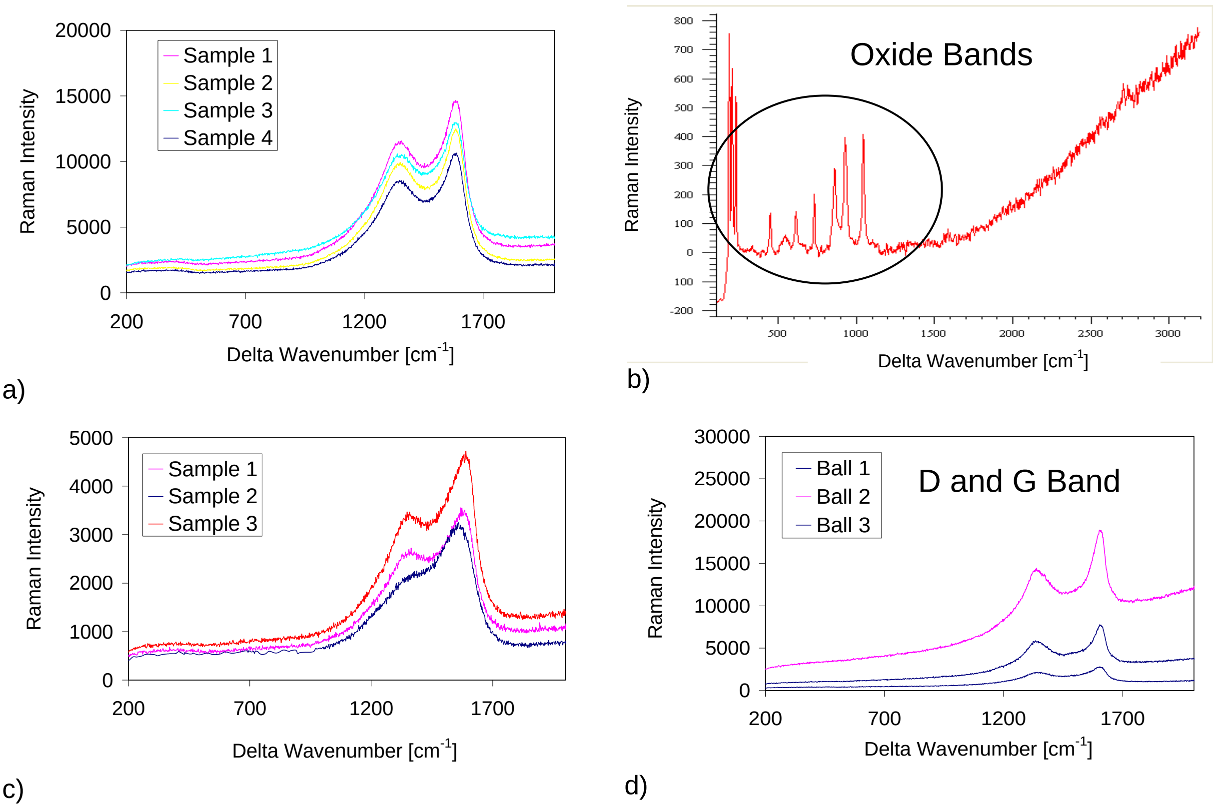


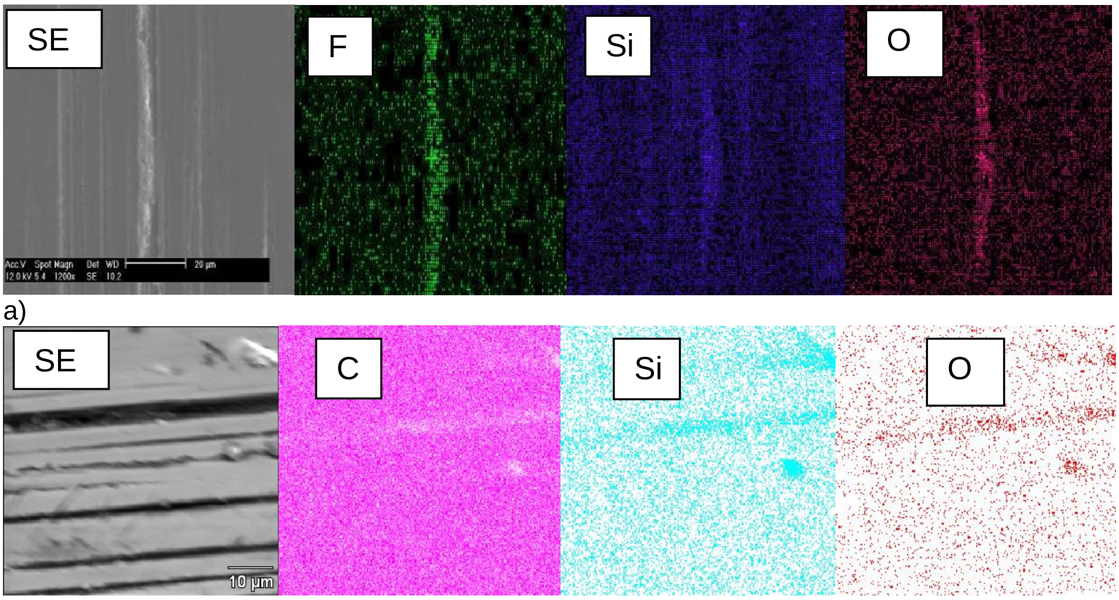
Figure 4: µRaman spectra a) HFC134a DLC samples; b) HFC134a Counter body; c) HC600a DLC samples; d) HC600a Counter body.

Raman spectroscopy of the wear scars of counter bodies tested in HC600a presented D and G bands of DLC indicating the contribution of the specimen (coating) to formation of a tribolayer. No oxide formations were verified on these analyses.

In the counter-bodies of HFC134a tests, Raman analysis presented many weak peaks in the range of 200 to 1000 cm^{-1} indicating formation of oxides, according to Sei et al.,(16) Ouyang and Hiraoka(17,18) and Scharf and Singer.(19) EDS elementary mapping were performed only on wear track and it confirms oxygen traces verified in Raman analyses.

Figure 5 shows elemental distribution at the wear scar for samples tested in HFC134a and HC600a atmospheres. It is clearly visible that there was material transfer between specimen and counter-body.

The results indicate contamination by atmospheric air in the test chamber and degradation of HFC134a refrigerant gas. On the contrary, the HC600a test results presented only Oxygen and Silicon traces, indicating only air contamination of the test chamber and test surfaces.



a)

b)

Figure 5: Micro analysis at the wear scars a) HFC134a samples; b) HC600a samples.

4 CONCLUSIONS

The coefficient of friction evolution of the HFC134a tests presented stable results in all of applied loads. The same behavior was observed in HC600a tests which presented lower coefficient of friction than HFC134a tests.

Comparing overall results, HC600a tests presented higher wear rate and lower durability than HFC134a tests. The differences were assumed as a result of the influence of the Fluorinated compounds, due to HFC134a degradation during tribological tests.

Raman spectroscopy of the wear scars of counter bodies tested in HC600a presented D and G bands of DLC indicating the contribution of the specimen (coating) to the formation of a tribolayer. No oxide formations were verified on these analyses.

In the counter-bodies of HFC134a tests, Raman analysis presented many weak peaks in the range of 200 to 1000 cm^{-1} indicating, according to the literature formation of oxides.

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