Original Article

Genesis and stability of tribolayers in solid lubrication: case of pair DLC-stainless steel☆

Diego Berti Salvaro[a],*, Márcio Silvério[b], Cristiano Binder[a], Renan Oss Giacomelli[a], Aloisio Nelmo Klein[a], José Daniel Biasoli de Mello[a]

[a] Materials Laboratory, Universidade Federal de Santa Catarina, Florianópolis, SC, Brazil
[b] Tribology Laboratory, Embraco, Joinville, SC, Brazil

ARTICLE INFO

ABSTRACT

The morphology, dimensions and chemical composition of tribolayers strongly depend on the pressures and temperatures acting on the contact. They are formed by reactions between surfaces in contact with each other as well as with the atmosphere, lubricants and possible contaminants. In this paper, the influence of test time (180, 500, 1000 and 2500 h) on the formation and characteristics of tribolayers in pairs of DLC-stainless steel that were tested under an atmosphere of refrigerant gas R134a and without lubricating oil was analyzed. The characterization was performed using scanning electron microscopy with energy dispersive spectroscopy (SEM-EDS) (morphology and chemical composition) and white light interferometry (thickness). The tribolayer thicknesses ranged from 100 to 500 nm, and they were composed of elements originating from mutual transfers between the tribological pairs, as well as oxides that were more pronounced on the stainless steel surface. The results show that the tribolayers are chemically stable, maintaining the same composition over time, and their thicknesses remained constant after 1000 h of testing.

1. Introduction

A considerable fraction of the energy generated in the world is lost due to friction and wear in mechanical systems. According to Jost [1], it is possible to reduce these losses by up to 20% through the application of existing knowledge and techniques.

Fluid lubrication is widely applied to reduce friction and wear. However, environmental factors will likely lead industries to reduce or even eliminate lubricating oils. Additionally, there are applications where the presence of oil is not feasible, e.g., environments of high temperature and pressure that promote chemical degradation. Contaminant-free systems such as those used for food and pharmaceutical equipment are
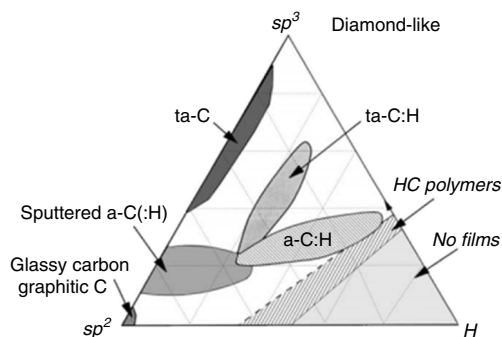

Fig. 1 – Ternary phase diagram for hydrogenated amorphous carbon alloys [3].
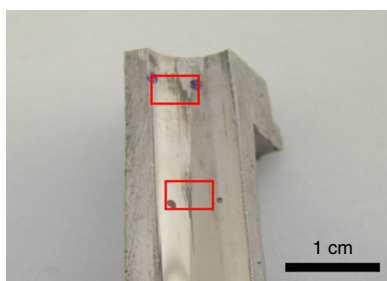
Fig. 2 – Possible tribolayers highlighted in red.

also applications where dry lubrication would be of benefit [2]. Therefore, improving the tribological performance of mechanical elements is a prerequisite for the development of new products and manufacturing processes [3].

Oil-less tribosystems represent a new challenge for the fields of surface science and engineering, stimulating new projects on coatings and self-lubricating materials. Amorphous or diamond-like carbon (DLC) coatings have been an implemented in many technological applications, such as, hard coatings for tools, automotive parts, computer hard

drives and microelectromechanical systems (MEMS). The applications are mainly associated with the material's hardness, chemical inertness and capacity as a solid lubricant [4]. DLC consists of hydrogenated amorphous carbon alloys (a-C:H), as shown by the ternary diagram in Fig. 1, where different families of DLC are characterized by their percentages of sp^2 and sp^3 hybridizations, and hydrogen content [5]. Doping elements are additionally incorporated into DLC to modify its properties such as silicon (a-C:H:Si), which decreases the free energy of the system and reduces residual stress in the coating by modifying its tribological behavior [6]. Other commonly used dopants for DLC include tungsten, titanium, molybdenum and chromium.

The low coefficient of friction associated with DLC is often attributed to the tribolayer formation, which mainly results from a transfer of material from DLC to the counterbody [6–8]. The genesis of these tribolayers is strongly dependent on the environment. For atmospheres such as air, oxygen or nitrogen, an increase of humidity usually reduces the friction coefficient of a DLC-steel contact [9,10]. In a study performed by de Mello, Binder et al. [11], it was shown that the presence of a protective atmosphere (R600a) modified the chemical structure of the tribolayer generated on the counterbody, thereby reducing the coefficient of friction and the wear rate of the system (DLC/steel AISI 52100). In another work performed by Demas and Polycarpou [12], pin-on-disk tests were performed using gray cast iron (pin and disk) without lubrication and under different atmospheres (O_2, CO_2, N_2, Ar and R134a). Under an O_2 atmosphere, the wear was governed by oxidation of the wear track, whereas in air and R134a, the wear also contained an adhesive component. Under a N_2 atmosphere, the wear was dominated by adhesion, whereas in CO_2, there was a slight polishing on the surface that removed only superficial asperities and resulted in the best tribological performance among the tested atmospheres.

The tribolayers settle on the real contact area and therefore dictate the tribological behavior of the tribosystems. Their dimensions are modified on the nanometer scale, and this

Height difference : 0.619 μm　　Height difference : 0.44 μm
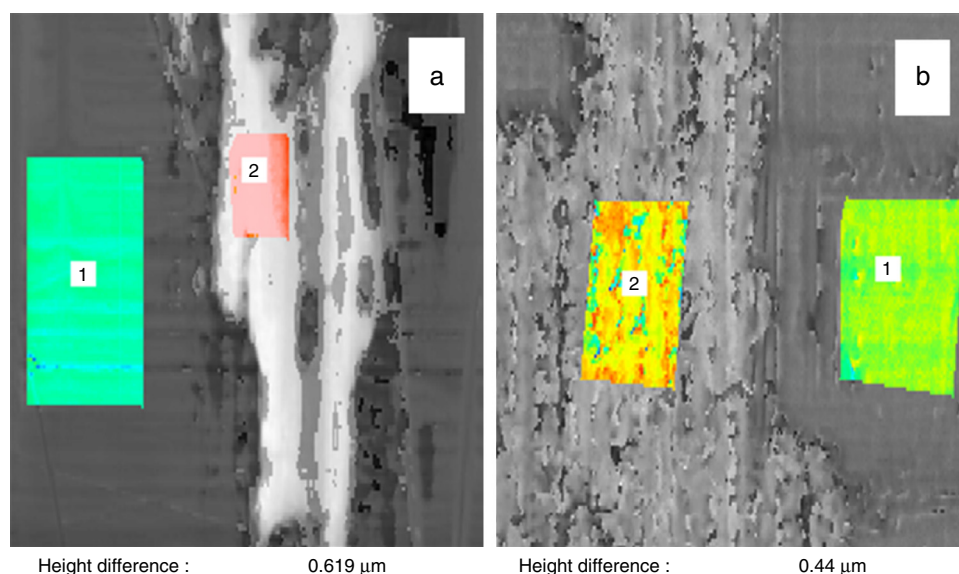
Fig. 3 – Examples of tribolayer thickness measurements on the stainless steel surface. (a) 500 h, and (b) 2500 h.

|	Secondary	Backscattered
180 h		
500 h		
1000 h		
2500 h		
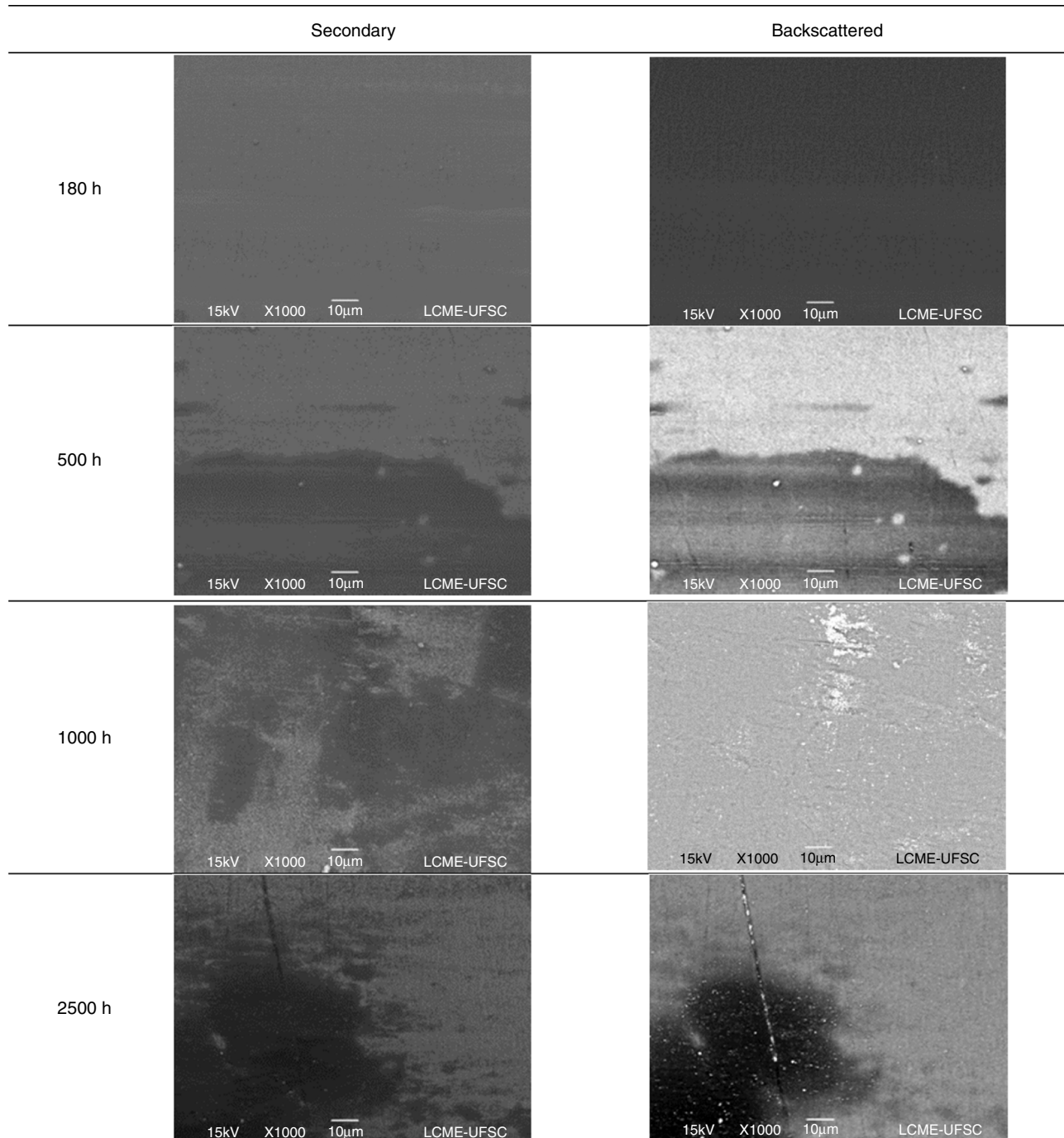
Fig. 4 – Scanning electron microscopy (SEM) images of tribolayers found in DLC.

factor complicates an understanding of their formation and stabilization. Tribolayers are formed from the physicochemical interactions between surfaces in contact and relative motion. Such interactions ranges from the mutual transfer of materials to reactions between atmosphere, lubricants and contaminants present in the region of contact [13].

The contact conditions affect the formation and destruction of tribolayers, i.e., the stability of tribolayers, depends of contact evolution. When the formation and destruction rates

of tribolayers acquire the same values, then the tribolayers achieve a certain mechanical equilibrium, which, from the point of view of tribological performance, is fundamental to contact stability.

The present study uses widely available characterization tools to evaluate mechanical and chemical long term (up to 2500 h at 350 Hz) stability of tribolayers on a specific pair DLC-stainless steel in a R134a refrigerant gas closed system.

	Secondary	Backscattered
180 h		
500 h		
1000 h		
2500 h		
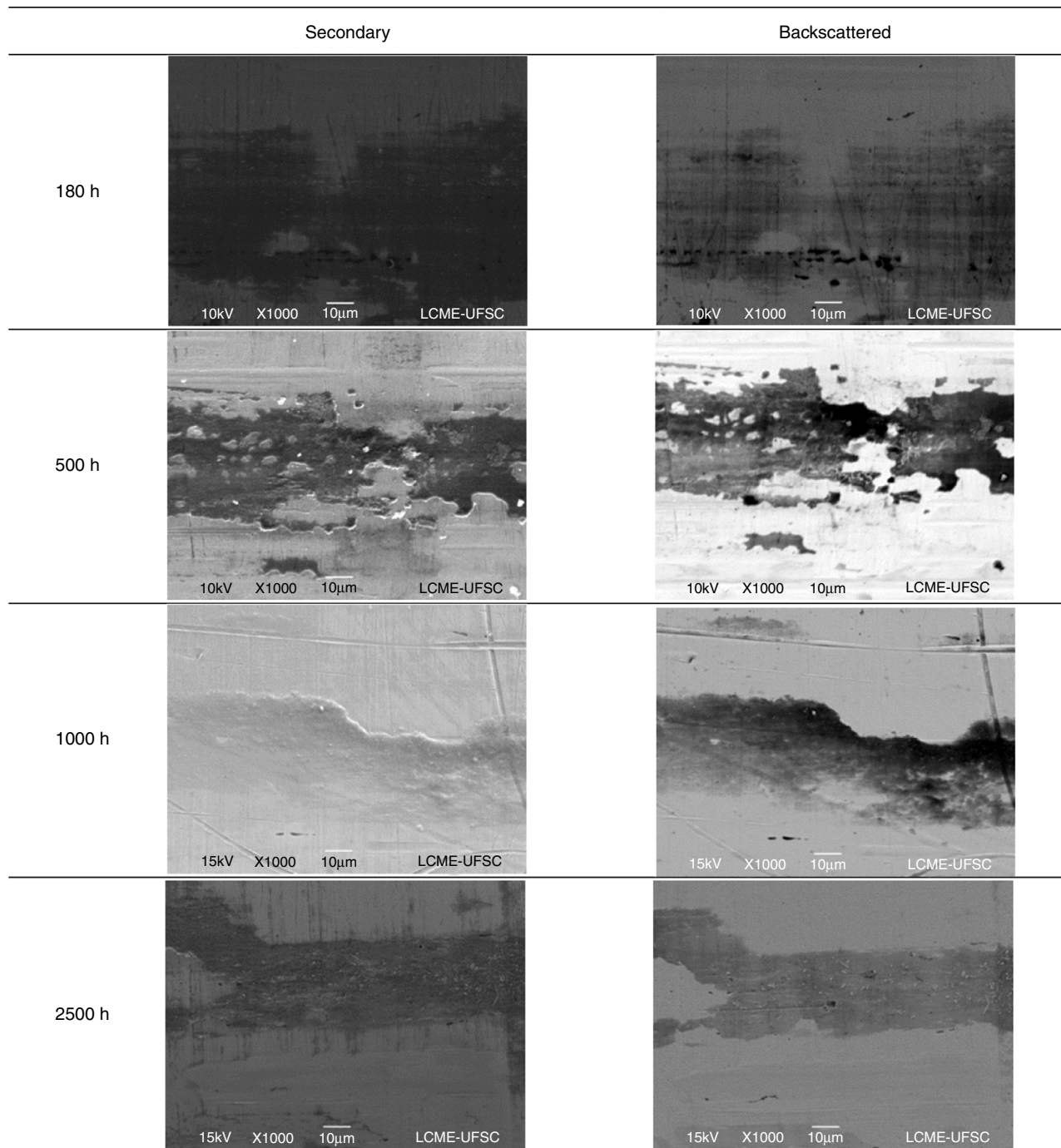
Fig. 5 – Scanning electron microscopy (SEM) images of tribolayers found in stainless steel.

2. Materials and methods

Tribological pairs were formed by a AISI 52100 multilayer [CrN (1.5–2.0 μm thick) – DLC (1.0 μm thick)] coated piston (ø = 10 ± 0.05 mm × L = 30 mm) and a AISI 304 stainless steel cylinder (ø = 10 ± 0.05 mm × L = 35 mm) coaxially coupled. The specially developed, proprietary tribometer was designed to impose a contactless reciprocating movement (1.7 mm amplitude and frequency of 350 Hz) in which there is no pre-defined contact pressure. However, since the clearances are very tide,

some misalignment occurs, which generates contact in random regions during movement of the piston. The lateral forces imposed are inferior to 15 N. The tests were carried out in a hermetic chamber that allows for strict control of the temperature (80° C) and atmosphere (21 Bar, tetrafluoroethane (R134a) refrigerant gas).

Nine experiments were conducted: three, each with duration of 180 h, and two each for periods of 500, 1000 and 2500 h.

Upon completion of the tests, the stainless steel cylinders were sectioned to provide access to the contact areas. Stainless steel cylinders and DLC coated pistons surfaces were
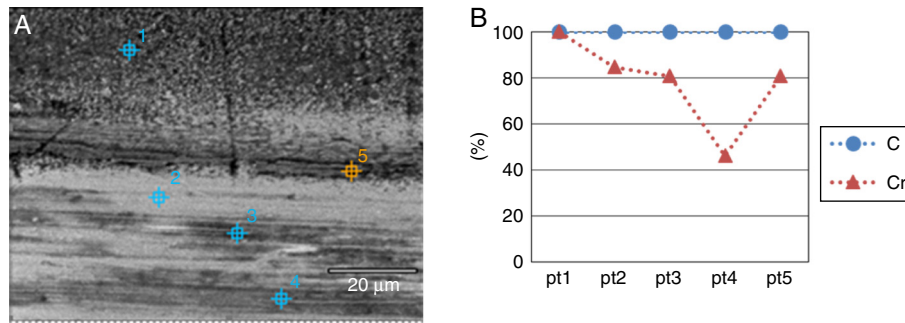
Fig. 6 – Variation of the carbon and chromium concentration outside (1) and inside (2, 3, 4, 5) of the tribolayer over DLC. (A) Measurement location. (B) Evolution of C and Cr concentrations.
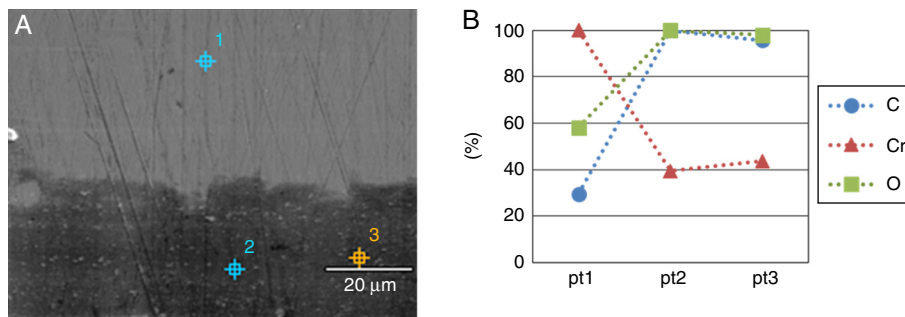
Fig. 7 – Variation of the carbon, chromium and oxygen concentration outside (1) and inside (2, 3) of tribolayer over stainless steel. (A) Measurement location. (B) Evolution of C, Cr and O concentrations.

cleaned with cotton and absolute ethyl alcohol. Generally speaking, locating and identifying tribolayers in the darker regions of the samples (highlighted in Fig. 2) should be easier.

The relevant regions were analyzed using scanning electron microscopy (SEM-JEOL JSM-6390LV).

For data acquisition of dimensional analysis, a white light interferometer (Zygo New View 7300) was used. MoutainsMap® software was employed to measure the average thicknesses of the tribolayers. The procedure consisted of selecting two regions, one within the tribolayer and a second on the original surface, then calculating the average height difference between these two regions. In Fig. 3, there are two examples of thickness measurements of tribolayers from two different tests (500–2500 h). Regions labeled 1 refer to the original surface, and those labeled 2 refer to the tribolayer. Height measurements were repeated five times at different points within each region.

3. Results and discussion

3.1. SEM and EDS

Figs. 4 and 5 provide SEM images of typical tribolayers present on DLC coated piston and stainless steel cylinder surfaces, respectively. Although tribolayers were found in both sides of the tribopair, they were more pronounced on stainless steel cylinder surfaces. On the left column, SEM images show that topographic details of tribolayers in both DLC coated piston (Fig. 4) and stainless steel cylinder surfaces (Fig. 5) differ from the original surfaces. Images in the right column of each figure were obtained using backscattered electron data and the contrast is indicative of variations in the average atomic number. The simultaneous analysis of the two aspects allows to evaluate both the morphological (including topographic) and chemistry evolution of the tribolayers.

For the case of the tribolayers formed on the DLC coated piston (Fig. 4) we note almost no tribolayer after testing for 180 h.

For 500 h testing the tribolayer is well formed with continuous and homogeneous aspect, while for longer times, it begins to be degraded and presents a thinner and increasingly fragmented aspect.
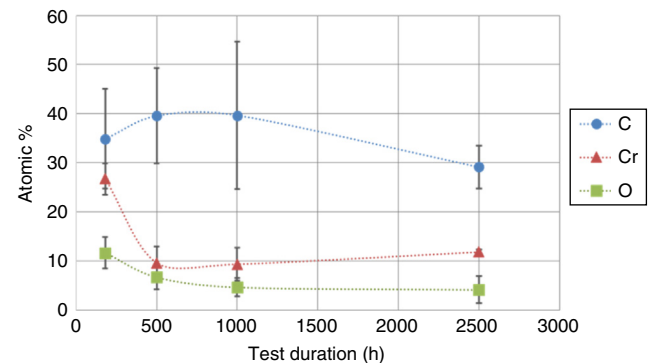
Fig. 8 – Evolution of carbon, chromium and oxygen concentrations with test duration for tribolayers found on stainless steel surfaces.
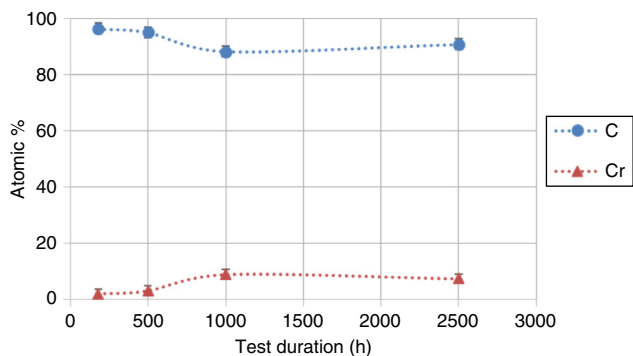
Fig. 9 – Evolution of carbon and chromium concentrations with test duration for tribolayers found on DLC surfaces.

Unlike, tribolayers formed in the stainless steel cylinder (Fig. 5), as already reported, are more pronounced and well developed even after 180 h test time. For the tests interrupted in 500 h the tribolayers are quite heterogeneous and fragmented, whereas, for longer test times the aspect becomes increasingly uniform and homogeneous.

The differences in concentration of carbon, chromium and oxygen outside and inside the tribolayer are displayed in Figs. 6 and 7. These values were obtained by dividing the value for each element by the highest observed concentration for each element (normalization). The carbon percentage on DLC coated piston surfaces varied very little over all examined regions (Fig. 6). However, the carbon content inside the stainless steel cylinder tribolayer was of note (Fig. 7), and its origin may be associated with material transfer from the DLC coating. The additional increased presence of oxygen in this tribolayer clearly indicated an oxidation process in accordance with the results of Wu, Pai and Hon [14].

Due to electron beam penetration, the substrate has a direct influence on the EDS results. A reduction of the chromium concentration on the contact regions of DLC coated piston occurred due to coating wear, which allowed more interaction between the electron beam and the substrate atoms (AISI 52100) below the CrN layer. The chromium concentration on tribolayers associated with the stainless steel cylinder decreased when compared with the original surface (Fig. 7).

Fig. 8 shows the evolution of carbon, chromium and oxygen concentrations with test time for tribolayers related to stainless steel cylinder surfaces. The atomic percentage of oxygen slightly decreased for test times up to 1000 h, after which the values remained almost constant. The same behavior was observed for chromium; however, the initial drop in signal was more abrupt and occurred between 180 and 500 h. In spite of the large dispersion presented by the amount of carbon, it was possible to observe a reverse trend in relation to the chromium evolution, indicating the formation of carbon-rich tribolayers that originated from the DLC coating. Fig. 9 shows the evolution of carbon and chromium concentrations with test time for tribolayers related to the DLC coated piston surfaces. The same inverse behavior between carbon and chromium
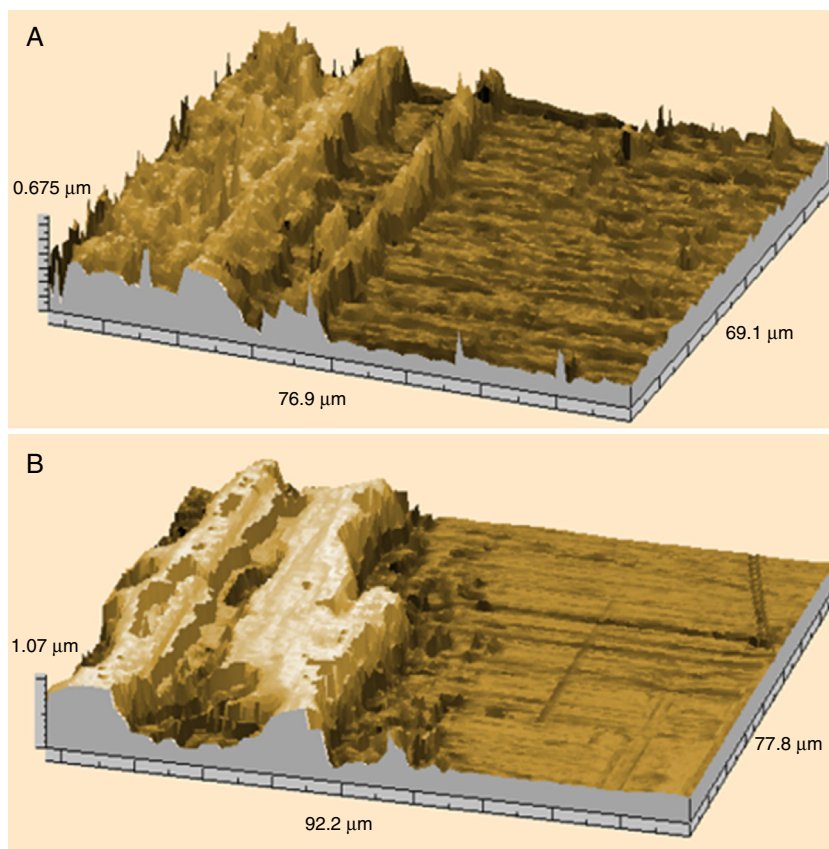
Fig. 10 – Tribolayers surface topographies on stainless steel surface: (A) 180 h and (B) 500 h.
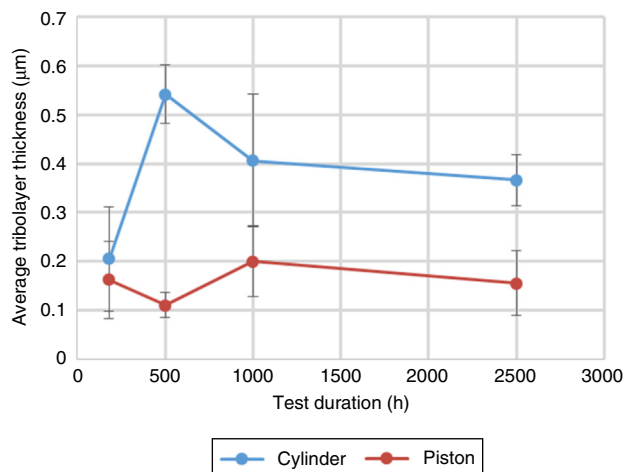
Fig. 11 – Average thicknesses of tribolayers on DLC and stainless steel.

concentrations was observed again, indicating a possible mutual transfer of material between the surfaces [15].

Tribo-reactions that gave rise to the tribolayers were active for up to a 1000 h of testing. After this time period, the tribolayers remained relatively stable in terms of their chemistry.

3.2. interferometry

Fig. 10 shows the surface topography of tribolayers after 180 and 500 h of testing. After 500 h, the tribolayer was thicker and showed large flat areas that were probably because of the relative motion between surfaces in accordance with the results of Olofsson et al. [16]

Fig. 11 shows the influence of the test duration on the thicknesses of the tribolayers. For extended test times (1000 h), the average thickness of tribolayers varied little and stabilized at a thickness of approximately 170 nm for DLC coated piston specimens and 380 nm for stainless steel cylinder samples. Between 180 and 500 h of testing, there was a significant increase in the average thickness of the tribolayers found on stainless steel cylinder from 200 to 500 nm; from 500 to 1000 h of testing the tribolayers decreased to an average thickness of 400 nm. The opposite trend was observed for tribolayers located on the DLC coated piston. These data suggest the formation and destruction of the tribolayers on both the body and the counterbody until 1000 h, after which the morphological modifications reached an equilibrium state.

4. Conclusions

The present study, using widely available characterization tools, evaluated mechanical and chemical long term (up to 2500 h at 350 Hz) stability of tribolayers on a specific pair DLC-stainless steel in a refrigerant gas R134a closed system. The main conclusions are:

1. The chemistry of the tribolayer (represented by the concentration of chromium, carbon and oxygen) presented a significant variation between 180 and 1000 h of testing. After that time, the tribolayers remained relatively stable in terms of their chemistries;

   The same general behavior was presented by the thickness of the tribolayer and resulted in a thicker layer on the stainless steel cylinder and a thinner layer on the DLC coated piston;

2. It is suggested that a mutual transfer of certain elements between the two surfaces is at the origin of a mutual destruction and formation of tribolayers until a stable state was eventually reached.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgments

REFERENCES

[1] Jost HP. Tribology: origin and future. Wear 1990:1–17.
[2] Schroeder R, Klein AN, Binder C, de Mello JDB. Internal lubricant as an alternative to coating steels. Met Powder Rep 2010:24–31.
[3] Zhiqiang F, Jian S, Chengbiao W, Wei Z, Wen Y, Zhijian P, et al. Tribological performance of DLC coatings deposited by ion beam deposition under dry friction and oil lubricated conditions. Vacuum 2013:14–8.
[4] Viana GA, Motta EF, da Costa MEHM, Freire FL Jr, Marques FC. Diamond-like carbon deposited by plasma technique as a function of methane flow rate. Diam Relat Mater 2010:756–9.
[5] Robertson J. Diamond-like amorphous carbon. Mater Sci Eng 2002:129–281.
[6] Donnet C. Recent progress on the tribology of doped diamond-like and carbon alloy coatings: a review. Surf Coat Technol 1998:180–6.
[7] Ronkainen H, Likonen J, Koskinen J, Varjus S. Effect of tribofilm formation on the tribological performance of hydrogenated carbon coatings. Surf Coat Technol 1996:87–94.
[8] Grill A. Review of the tribology of diamond-like carbon. Wear 1993:143–53.
[9] Lifang X, Guang L. The frictional behavior of DLC films against bearing steel balls and Si3N4 balls in different humid air and vacuum environments. Wear 2008:1077–84.
[10] Erdemir A, Bindal C, Pagan J, Wilbur P. Characterization of transfer layers on steel surfaces sliding against diamond-like hydrocarbon films in dry nitrogen. Surf Coat Technol 1995:559–63.
[11] de Mello JDB, Binder R, Demas NG, Polycarpou AA. Effect of the actual environment present in hermetic compressors on the tribological behaviour of a Si-rich multifunctional DLC coating. Wear 2009:907–15.
[12] Demas NG, Polycarpou AA. Tribological investigation of cast iron air-conditioning compressor surfaces in CO$_2$ refrigerant. Tribol Lett 2006:271–8.

[13] Luo Q, Zhou Z, Rainforth WM, Bolton M. Effect of tribofilm formation on the dry sliding friction and wear properties of magnetron sputtered TiAlCrYN coatings. Tribol Lett 2009:113–24.

[14] Wu WJ, Pai TM, Hon MH. Wear behavior of silicon-containing diamond-like carbon coatings. Diam Relat Mater 1998:1478–84.

[15] Suzuki M, Saito T, Tanaka A. Tribological properties of DLC films against different steels. Wear 2013:83–7.

[16] Olofsson J, Gerth J, Nyberg H, Wiklund U, Jacobson S. On the influence from micro topography of PVD coatings on friction behaviour, material transfer and tribofilm formation. Wear 2011:2046–57.