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TRIBOLOGICAL ASSESSMENT OF CARBON NANOTUBES FILMS PRODUCED BY PLASMA-ENHANCED CHEMICAL VAPOUR DEPOSITION: A COMPARISON BETWEEN DRY AND WET CONDITIONS

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Abstract. Recent studies conducted in the field of tribology have shown that lubrication and wear protection can significantly reduce CO_2 emissions increasing energy savings. Carbon-derived materials could be potential solutions to reduce friction and wear, acting as solid lubricants. Besides the dry conditions performance, the behavior of carbon nanotubes film in wet conditions is little explored. This work studied the potential of carbon nanotubes (CNT) films obtained via plasma-enhanced chemical vapor deposition (PECVD) as lubricant in a wet condition (with 5 μl of oil). Morphological and structural aspects of the surfaces were assessed by scanning and transmission electron microscopy and Raman spectroscopy. Tribological characterization was performed using dry and wet conditions, constant and variable load reciprocating sliding tests. The developed surfaces consisted of a regular cementite layer (Fe_3C) and a CNT film. The CNTs morphologies showed bamboo-like structures able to reduce the friction coefficient from 0.3 to 0.1 at dry conditions. The layer thickness of the Fe_3C also was relevant to the tribosystem behavior. The synergy between CNT film and oil showed better results in terms of wear resistance compared to the non-CNT film in the wet conditions. Overall, the addition of oil decreased the tribological performance of the CNT films.

Keywords: Carbon nanotubes, PECVD, tribology, wear, lubricity

1. INTRODUCTION

In recent years, with the increasing concern for the environment, research on environmentally friendly lubrication methods has grown in volume and economic importance. Data indicate that costs related to friction and wear amount to around 973 million euros (Holmberg et al., 2017). The development of surfaces, materials, and lubrication technologies can reduce friction and wear losses by up to 40% in the next 15 years (Holmberg et al., 2017), (Woydt, 2021). Since the discovery of fullerenes in the 1980s, nanostructures of carbonaceous materials have shown good lubrication properties and, therefore, have attracted attention in tribological applications (Zarbin and Oliveira, 2013), (Binder et al., 2017), (De Mello et al., 2018). For this reason, nanostructured carbonaceous materials, such as carbon nanotubes, have received special attention in the field of tribology in the last decade.

Recently, carbon nanotubes have become a very promising research subject. The properties of electrical and thermal conductivity, along with good mechanical properties, are highly attractive for various areas such as information technology, medicine, among others. Various methods are currently employed in the synthesis of carbon nanostructures. The method used in this work is Plasma Enhanced Chemical Vapor Deposition (PECVD), a technique widely used in the Materials Laboratory (Labmat - UFSC) and with extensive potential for industrial application.

Differently of the common CVD process, the PECVD promotes an environment with a high kinetic energy and reactivity of the species allowing for obtaining results at lower temperatures (Terasawa et al., 2012). With the high energy involved, the dissociation of the carbon precursor occurs. In the case of methane, for example, it dissociates into various species, such as free carbon and hydrogen gas. Articles and publications on the formation of carbonaceous films highlight metal dusting, a corrosion phenomenon commonly observed in treatments involving reactive carbon with a catalytic substrate, as actively present in carbon nanotube synthesis (Zeng et al., 2001). The degradation reaction of carbides results in a metallic phase and a carbonaceous phase. As demonstrated by Zeng et al. (2001), metal dusting occurs between

temperatures of 400 °C to 900 °C in an atmosphere of active carbon on catalytic substrates such as iron, cobalt, and nickel, for instance.

According to Zeng et al. (2001), when a carbon atom reaches the surface, two paths can be observed: the atom can accumulate on the surface of the catalytic substrate, generating small carbon particles and consequently less crystallized carbon; or carbon can diffuse, forming cementite if the substrate is made of iron or steel. Thus, the subsequent carbon atoms would diffuse through the cementite, resulting in a more crystallized carbon in the cementite layers. Above this layer of cementite, the nanotubes grow by utilizing catalytic particles such as cementite, molybdenum, iron, among others (González et al., 2011), (Kumar, 2010). The growth of multi-walled carbon nanotubes can initiate with the catalytic particle, in this case, cementite particles generated by metal dusting, being enveloped by a graphene sheet on the substrate's surface. As more graphene sheets surround the particle, increasing pressure is generated until the particle jumps, initiating a new process of graphene sheet encapsulation on the particle, as shown by Kumar, (2010).

The tribological properties of carbon nanostructures have attracted interest in recent years, as demonstrated in studies by (Rui, 2014), (Zhai et al., 2017). The lubrication mechanism promoted by these nanostructures is a combination of phenomena such as rolling, sliding, and lubrication based on the graphite system, with the latter being promoted by the deformation and delamination of nanotubes along the tribological contact. Noneless, the addition of oils in tribological systems with carbonaceous films deposited on a metallic surface has been little explored until now. A significant portion of the literature (Liu et al., 2011), (Rui, 2014), (Cornelio et al., 2016), (Ye et al., 2019), focuses on particle dispersion in emulsions or solid lubrication applications. The tribological behavior of a high concentration of vertically aligned multiwalled nanotubes adhered to the surface, in the presence of lubricating oil, is unknown. In this context, the relevance of the current research proposal is justified, which aims to investigate the tribological performance, both in dry conditions and with the addition of a lubricating oil, of carbon nanotube films grown directly on catalytic surfaces of AISI 1005 steel via PECVD.

2. EXPERIMENTAL PROCEDURE

The experimental procedure is divided into 2 steps: The first step is the production of the carbon nanotube films via plasma-enhanced chemical vapor deposition on a AISI 1005 steel substrate. The surface of the steel samples was polished, to uniformize the topography of the samples. The plasma treatment was conducted in a plasma reactor in a confined anode-cathode configuration as detailed in the patent published in 2016 (Binder et al., 2016). With the objective to obtain two different morphologies, the parameters were defined as shown in Table 1. The definition of parameters such as temperature, DDP, pressure, atmosphere, frequency of pulse, duty cycle and gas flow, was based on the Doctoral thesis of Thiago de Souza Lamim (Lamim, 2021). In Table 1, the names CNT-M1 and CNT-M2 are referred to carbon nanotubes films - morphology 1 and 2, respectively.

Table 1. Treatment parameters

	Step	t (min)	T (°C)	DDP (V)	P (Torr)	F (Hz)	Gas Mixture	Duty cycle (%)	Gas flow (sccm)
CNT M1	Heating	65	0-700	400	2.5	10	100% H_2	40	200
	Level	180	700	650	2.5	7	60% H_2/ 40% CH_4	75	200
CNT M2	Heating	65	0-600	600	2.5	10	100% H_2	40	200
	Level	180	600	650	5.0	7	60% H_2/ 40% CH_4	25	400

The characterization of the two morphologies of carbon nanotube films obtained was performed using a Renishaw micro-Raman, model 2000, equipped with an Argon laser (514.5 nm). The shape and diameter of the nanotubes were evaluated using a scanning electron microscope (VEGA3 LMU, Tescan). A transmission electron microscope (TEM) model JEOL JEM 1011 operating at 100 kV in bright field mode was used for high magnification images. The nanotubes were detached from the specimen surface using an ultrasonic probe tip (SONICATOR S4000) in an isopropyl alcohol bath for this analysis. Then, the analysis material was dripped onto a copper grid covered with amorphous carbon.

Tribological characterization was carried out in a reciprocating sphere on cup configuration using a CTR UMT-2 tribometer in ambient conditions, with humidity (45 ± 10%) and temperature (22 ± 2 °C). The counter body was AISI 52100 steel ball with 5 mm diameter, the wear track was 10 mm long and the reciprocating movement frequency was 2 Hz. The tests were performed in constant load wear tests using a normal load of 7 N for 60 min. The objective of these tests was to compare the coefficient of friction and wear rates of the system as a function of the presence of two different morphologies of carbon nanotubes films.

In addition to the dry tests, oil lubricated tests were also performed. In those tests, 5 µl of a low viscosity alkylbenzene oil (4.1 - 4.8 cSt at 40 °C) was applied on the plane surface before the contact. The wear volume of the samples was

obtained with profilometry (10 profiles per mark) and the data acquired was analyzed using the software Mountains Map v7.1. Additionally, the wear scars were analyzed using a scanning electron microscope (SEM) coupled with an energy dispersive spectroscopy (EDS) probe (VEGA3 LMU, Tescan). The counter-bodies were also ultrasonically cleaned and then observed through optical microscopy. The wear rates of the counter-bodies were obtained by measuring the cap diameter formed in the sphere with the aid of image analysis software.

3. RESULTS AND DISCUSSION

3.1 Validation of different morphologies

As described in the literature, the growth of carbon nanotubes on catalytic iron surfaces primarily starts with the most saturated carbon layer on the surfaces, where cementite particles are present. Figure 1 shows SEM images of the cementite layers formed under conditions to morphology 1 (Figure 1a) and morphology 2 (Figure 1b). The CNT-M1 samples exhibited a cementite layer size of 2.45 μm, more than twice as large as the CNT-M2 samples (1.01 μm). The growth of the layer is related to the level temperature and carbon supply during the process, which is higher in both cases to CNT-M1, thereby increasing carbon diffusivity.
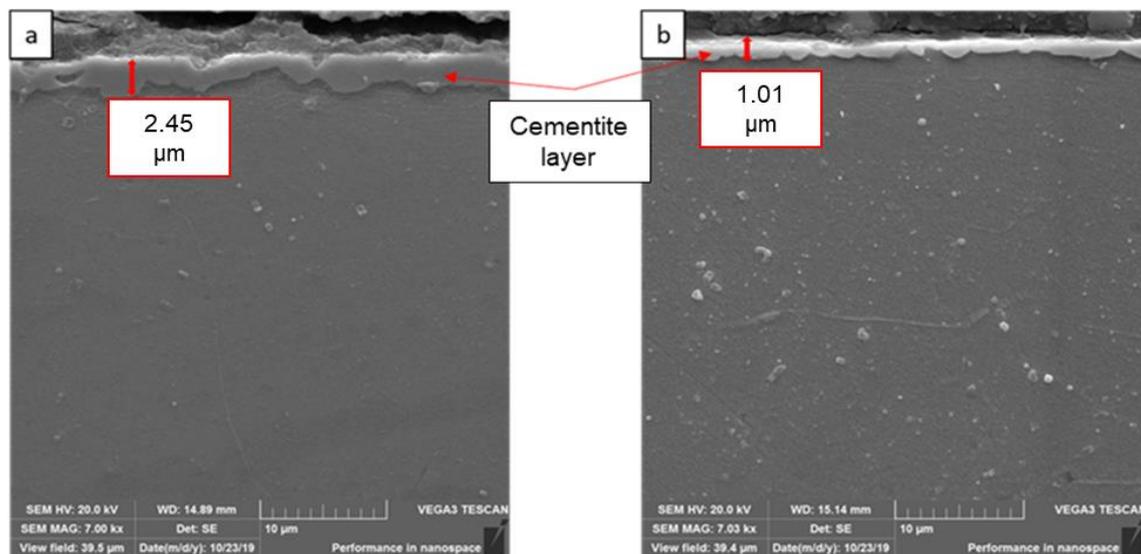

Figure 1. SEM images of the cementite layers of the CNT-M1 (a) and CNT-M2 (b) samples.

This cementite layer, with varying thicknesses, is responsible for the difference in size between the catalytic particles that are encapsulated by carbon sheets (graphene), a mechanism known as metal dusting. The driving force for metal dusting includes conditions of temperature (400 to 800 °C) and atmosphere (carbon activity greater than 1) that induce a superficial disintegration of the cementite layers, consequently generating catalytic cementite/iron seed nanoparticles onto the surface that will be responsible for the nucleation and growth of the carbon nanotubes (Kumar, 2010), (González et al., 2011). Figure 2 shows the nanotubes obtained for both conditions, in SEM and TEM images. In Figure 2(a), the CNT-M1 nanotubes, when compared to the CNT-M2 nanotubes in Figure 2(b), appear to have longer and wider nanotubes. In fact, measurements performed on these nanotubes revealed that the CNT-M1 morphology had an average length of 6.92 ± 1.34 μm and an average diameter of 0.17 ± 0.03 μm, while the CNT-M2 morphology had an average length of 2.08 ± 0.46 μm and an average diameter of 0.06 ± 0.01 μm. Therefore, the CNT-M1 samples exhibited nanotubes that were approximately 3 times larger than those of CNT-M2.

The significantly larger dimensions of the CNT-M1 morphology were attributed to the longer plasma-on time, which is related to the duty cycle parameter and accounts for 75% of the cycle time in the CNT-M1 morphology. This extended plasma-on time significantly increases the carbon supply on the surface and, consequently, promotes the growth of the nanotube length (Lamim, 2021).

To evaluate the morphology of the formed carbon nanotube films, highlighting differences beyond the nanotube size, Raman spectroscopy was able to provide relevant results. The spectra resulting from the Raman analysis are compiled in Figure 3, along with a table containing the main band ratios. As elucidated by Antunes et al. (2007) and Costa et al. (2008), the full width at half maximum (FWHM) of the G and 2D bands is sensitive to the structural ordering and diameter of the nanotubes, where narrower bands (smaller FWHM) indicate higher ordering. The table below the spectra in Figure 3 indicates that CNT-M1 exhibits a higher structural ordering, with an I2D/ID ratio of approximately 1.03 (higher than

CNT-M2). The greater ordering of CNT-M1 is also observed in the FWHM of the G and 2D bands, with values of 39.97 and 69.57, respectively, which are smaller than those observed in CNT-M2.

From this set of characterizations, it can be concluded that the nanotubes obtained under the CNT-M1 condition are larger, with greater structural order and a thicker layer of cementite, which in turn results in larger catalytic particles. In short, the CNT-M1 test conditions present a significantly greater amount of material available in the film, both in carbonaceous form and due to the presence of larger catalytic particles.
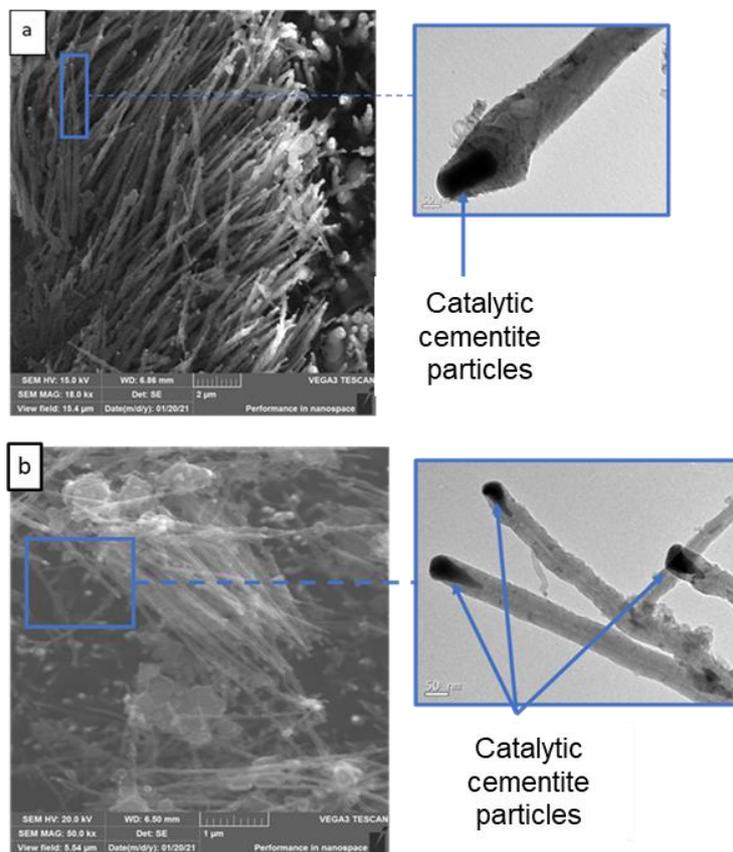

Figure 2. SEM and TEM images of the carbon nanotubes obtained from CNT-M1 (a) and CNT-M2 (b).
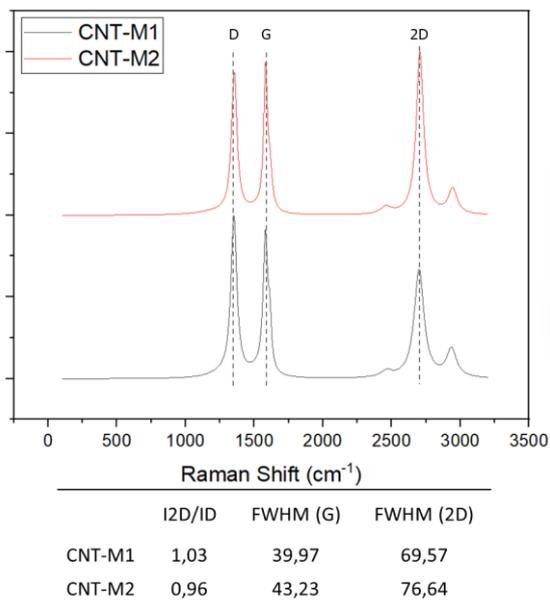

	I2D/ID	FWHM (G)	FWHM (2D)
CNT-M1	1,03	39,97	69,57
CNT-M2	0,96	43,23	76,64

Figure 3. Raman spectra of the morphologies produced (CNT-M1 and CNT-M2), and table with I2D/ID, FWHM (G) and FWHM (2D).

3.2 **Tribological behavior (Wear)**

The films of carbon nanotubes were subjected to tribological wear resistance tests, detailed in the experimental procedure. An important information obtained from the tribological pair, with and without oil, is the coefficient of friction. Figure 4 presents the results for the friction coefficient under steady-state conditions. Compared to the reference AISI 1005 steel, both tested conditions (CNT-M1 and CNT-M2) show a similar friction coefficient, around 0.1, with and without oil, with the CNT-M1 wet condition having the lowest friction coefficient.
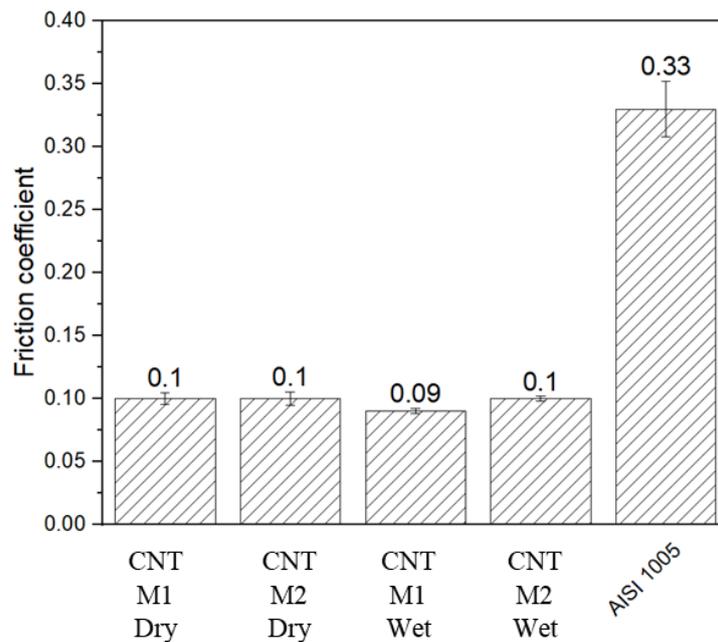

Figure 4. Friction coefficient friction in the steady-state regime of the tested conditions.

The performance difference, in terms of friction coefficient, indicates the existence of a synergy between carbon nanotubes and oil, even with small quantities of oil and in fact, the addition of oil in small quantities doesn't appear to produce any major difference in terms of friction. However, when evaluating the wear rates of the samples and counter bodies (Figure 5(a) and (b), respectively), the behavior is reversed, with the oil tests showing higher wear than the dry tests. This effect, shown in Figure 5 for both systems (samples and respective counter bodies), suggests that the carbon nanotube film itself is more efficient in generating protection against wear in the tribosystem than the oil + nanotubes.

Another factor is the lower wear of the samples, generally being an order of magnitude lower than the wear of the counter bodies. This suggests a protection generated by the mass of carbon provided by the nanotubes, as well as the sliding of the catalytic particles reducing friction and consequently wear. The standard deviation observed in the CNT-M1 dry condition may be linked to the interaction of these catalytic particles, larger in this condition, with the contact between the bodies, generating a range of performance for wear marks.
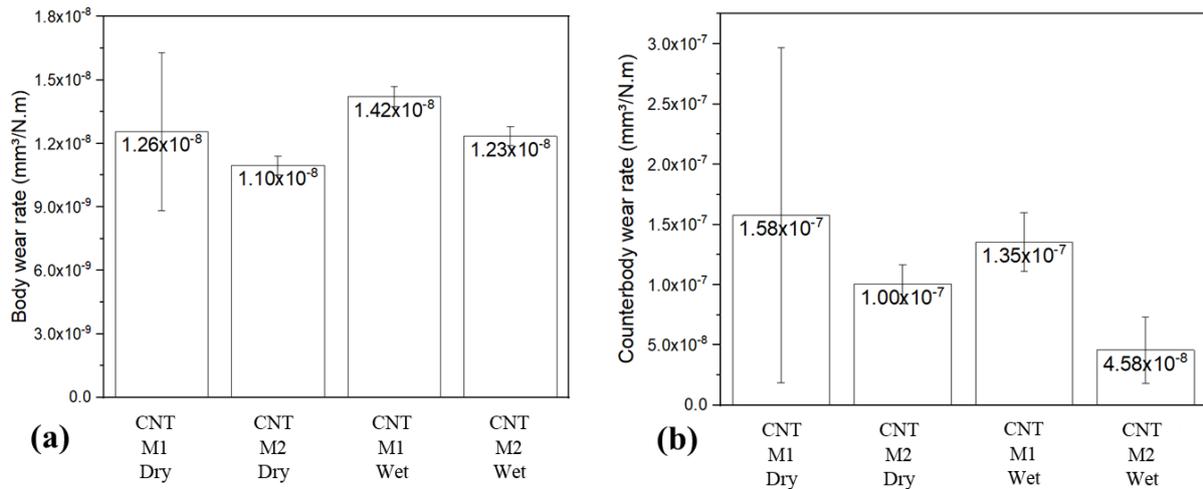
Figure 5. (a) Samples wear rates (mm³/Nm) and (b) counter body wear rates (mm³/Nm).

Finally, it can also be affirmed that the CNT-M2 morphology presented a higher wear reduction capacity, having a lower wear rate both in the samples and the counter body, another result that can be related to the size of the catalytic particles in each condition. In summary, the results indicate that wear may be associated with the size of the cementite particles catalyzing the nanotubes.

The wear marks on the CNT-M1 and CNT-M2 samples tested under dry and wet conditions can be observed in Figure 6. As noted by the authors Anselmo et al., (2022), the presence of carbon in tribological contacts plays a key factor in reducing friction and wear, regardless of the origin and ordering of this carbon. As the contact pressure is high in this test model, around 1.4 GPa, in the initial moments the nanotubes are crushed and comminuted, spreading this carbon across the wear mark, as can be seen in Figure 6.
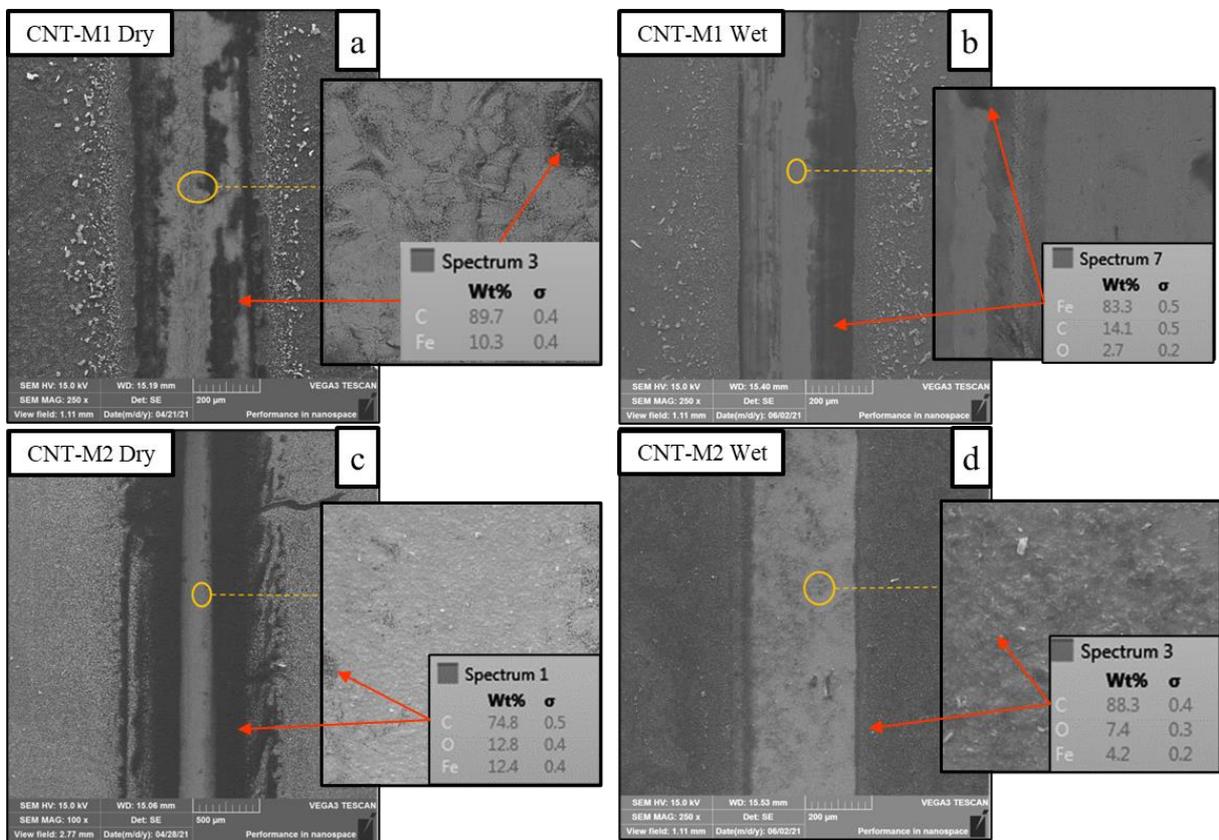

Figure 6. SEM and EDS analysis of the wear marks for the four tested conditions (a) CNT-M1 dry, (b) CNT-M1 wet, (c) CNT-M2 dry and (d) CNT-M2 wet.

The distribution of carbon differs between the dry tests and the tests with 5 µl of oil. In the dry tests, especially in CNT-M1, Fig. 6 (a) and (b), carbon layers are observed in the wear marks, serving as reservoirs that feed the contact with the lamellar solid, generating carbon shear mechanisms that reduce friction. In the case of oil tests, the wear marks show a buildup of carbon at their edges, as evident in Figure 6 (b). This suggests that the oil washes the mark, pushing the carbon towards the edges and promoting friction reduction.

The formed tribolayers also exhibit oxygen in their composition, commonly found in wear marks. These tribolayers significantly contribute to the wear and friction reduction process by generating an adhesive material that deposits to protect the contacting surfaces. Another important distinction between dry and oil-based tests pertains to the generated debris. These wear particles can be easily observed outside the wear marks, on their sides, whereas they cannot be observed in oil-based tests. This indicates that the oil mixes the carbon particles and catalytic particles with debris, generating a mass of material that protects the substrate from wear and reduces friction.

Finally, Figure 7 presents the wear marks of the 52100 steel counter bodies obtained through optical microscopy. In these images, it can be observed that the amplitude of the wear marks is similar for both morphologies, regardless of whether the conditions are wet or dry. The highlighted tribolayers, indicated by the red arrows, exhibit distinct formations. In the dry tests, for both CNT-M1 and CNT-M2, the formed tribolayers accumulated at the edges of the marks, whereas in the presence of oil, the tribolayer formation occurred at the center of the wear mark. Analogously, this effect can be related to the SEM images obtained and presented in Figure 6, where the opposite was observed. It is concluded that the carbon mass generates a protective tribolayer on the samples and counter body, which is carbon-rich. Additionally, the washing effect promoted by the presence of oil leads to carbon accumulation at the edge of the samples wear marks, while the continuous carbon supply deposits an adherent tribolayer at the center of the 52100 sphere's wear mark.
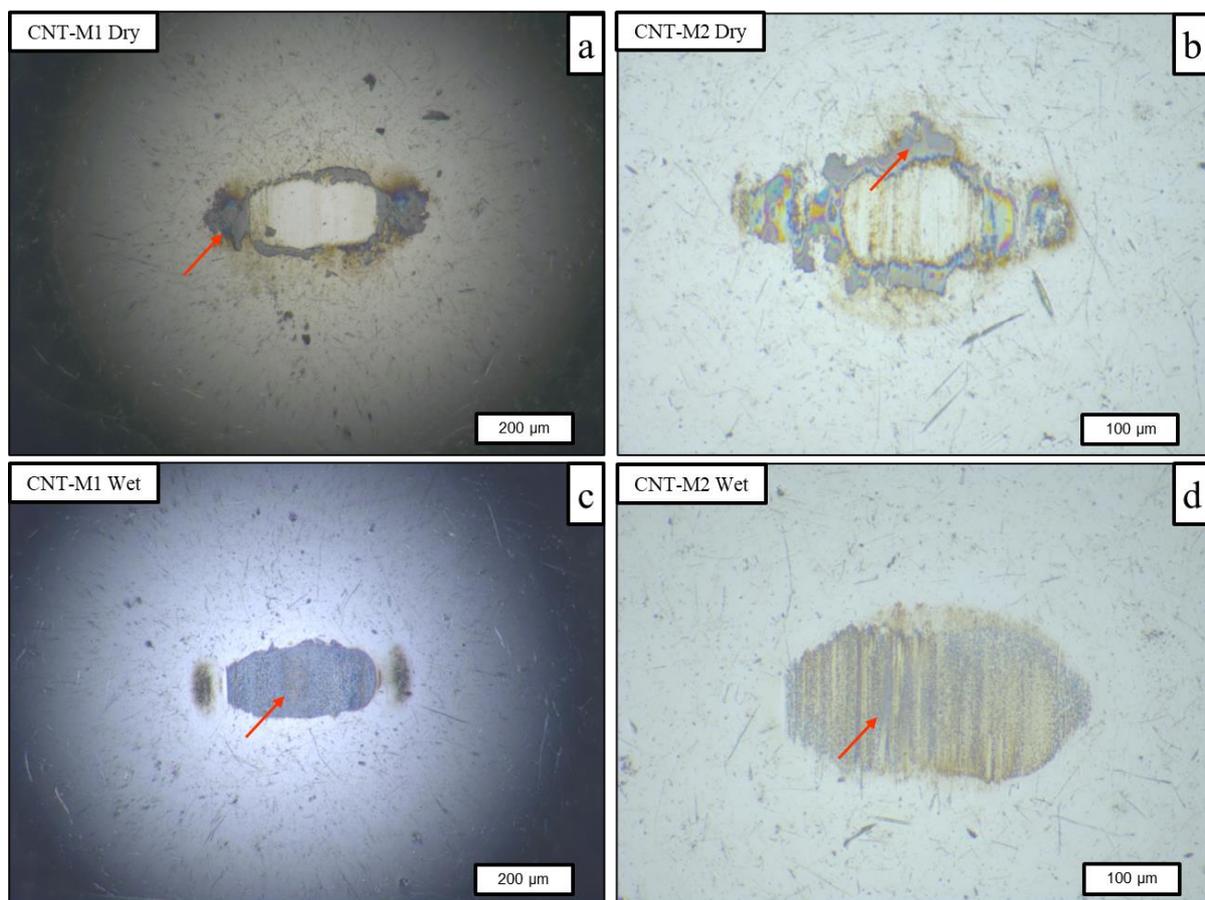

Figure 7. Images of the wear marks of the counter bodies obtained after the tribological tests (a) CNT-M1 sample in dry condition, (b) CNT-M2 sample in dry condition, (c) CNT-M1 sample in wet condition, (d) CNT-M2 sample in wet condition.

4. CONCLUSION

As demonstrated throughout the work, the obtained carbonaceous films exhibit a large quantity of carbon nanotubes, as observed through scanning electron microscopy images. These nanotubes are arranged on a cementite layer and are obtained through the metal dusting mechanism. The tips of these nanotubes also feature cementite particles, observed through TEM analysis, related to the growth of CNTs, where the particle is enveloped by carbon sheets.

Measurements carried out via SEM, both in the length and diameter of the nanotubes and in the cemented layer, indicate the presence of larger nanotubes in terms of diameter and length, as well as a thicker cemented layer in CNT-M1, because of the extended plasma-on time and carbon offer.

In Raman spectroscopy, a characteristic distinction in the presence of nanotubes in both morphologies was also noted. The intensity values of the 2D peak closely resemble values attributed to carbon nanotubes in the literature (Antunes et al., 2007). CNT-M1 exhibits greater structural ordering compared to morphology 2, identified by the indices obtained from the characteristics of the Raman shift bands, namely I2D/ID, FWHM (G), and FWHM (2D).

The tribological behavior in constant load tests indicated stable and low friction coefficients, with values of 0.1 throughout the test for both morphologies of carbon nanotube films. The wear tracks in both situations, evaluated via SEM, exhibit some differences between dry and oil conditions. While the dry track shows accumulated carbon residues in its center, the oil track displays a significant accumulation of carbon and oil on the sides of the track and a protective film in the center of the track, in both conditions.

The wear rate of the specimen was slightly higher in CNT-M2. The dry condition showed the least wear, which suggests that the nanotubes increase wear when oil is added to the film. The same applies to the counter body, indicating that the nanotubes provide greater protection to the counter body and that the addition of oil, even in small quantities, hampers their performance.

5. ACKNOWLEDGEMENTS

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